U.S. DEPARTMENT OF COMMERCE

PB80-169352

The Development of an Aqueous Trace Organic Standard Reference Material for Energy Related Applications

(U.S.) National Bureau of Standards
Washington, DC

Prepared for

Environmental Protection Agency
Washington, DC

Feb 80

U.S. Department of Commerce
National Technical Information Service
NTIS

NBS
EPA

U.S. Department of Commerce
National Bureau of Standards
Center for Analytical Chemistry
Washington, DC 20234

United States Environmental Protection Agency
Office of Environmental Engineering and Technology
Washington, DC 20460

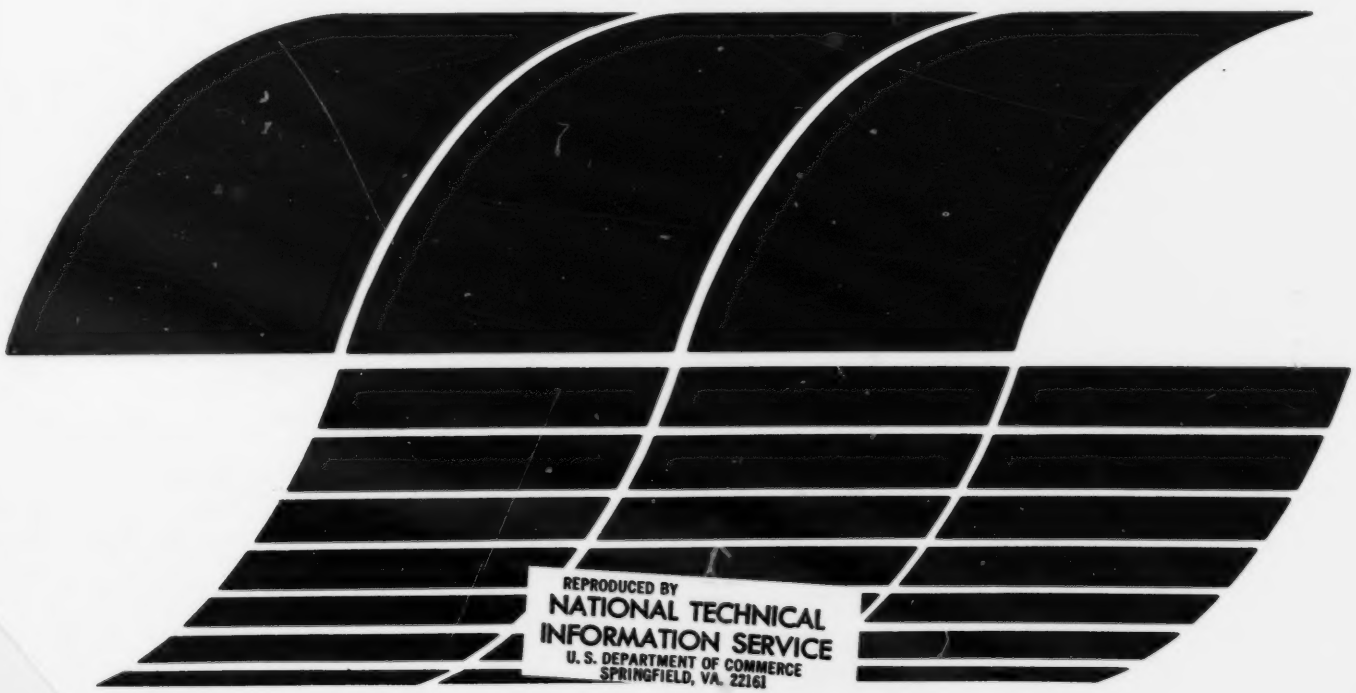
EPA-600/7-80-031
February 1980

Research and Development

PB80-169352

Development of an Aqueous Trace Organic Standard Reference Material for Energy Related Applications

Interagency Energy/Environment R&D Program Report



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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-80-031	2.
3. RECIPIENT'S ACCESSION NO. PB 80 169352	
4. TITLE AND SUBTITLE The Development of an Aqueous Trace Organic Standard Reference Material for Energy Related Applications: Investigation of the Aqueous Solubility Behavior of Polycyclic Aromatic Hydrocarbons	5. REPORT DATE February 1980
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Willie E. May	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Center for Analytical Chemistry, National Bureau of Standards, Washington, DC 20234	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency, Office of Research & Development, Office of Energy, Minerals & Industry, Washington, DC 20460	13. TYPE OF REPORT AND PERIOD COVERED Interim - Nov. 76- May 78
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
This project is part of the EPA-planned and coordinated Federal Interagency Energy/Environment R&D Program.

16. ABSTRACT

The development of a Standard Reference Material for aqueous solutions of known concentration of polynuclear aromatic hydrocarbons is an extremely difficult procedure. This paper is one of a series discussing the development of a generator column technqiue at NBS for the production of Standard Reference Materials for PAH's in water. In addition to providing the basis for SRM development the aqueous solubility is a fundamental parameter in assessing the extent and rate of the dissolution of energy based polynuclear aromatic hydrocarbons and their persistence in the aquatic environment.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
	20. SECURITY CLASS (This page)	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/7-80-031
February 1980

THE DEVELOPMENT OF AN AQUEOUS TRACE ORGANIC STANDARD REFERENCE MATERIAL FOR ENERGY RELATED APPLICATIONS: INVESTIGATION OF THE AQUEOUS SOLUBILITY BEHAVIOR OF POLYCYCLIC AROMATIC HYDROCARBONS

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Interagency Agreement No. EPA-IAGD5-E684

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Washington, DC 20460

This study was conducted
as part of the Federal
Interagency Energy/Environment
Research and Development Program

Prepared for

OFFICE OF ENERGY, MINERALS, AND INDUSTRY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

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FOREWORD

The role of the National Bureau of Standards (NBS) in the Interagency Energy/Environment R&D program, coordinated by the Office of Research and Development, U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by a wide variety of Federal, state, local, and private industry participants in the entire program. The work at NBS is under the direction of the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry, the Center for Radiation Research and the Center for Thermodynamics and Molecular Science. NBS activities are in the Characterization, Measurement, and Monitoring Program category and addresss data quality assurance needs in the areas of air and water measurement methods, standards, and instrumentation. NBS outputs in support of this program consist of the development and description of new or improved methods of measurement, studies of the feasibility of production of Standard Reference Materials for the calibration of both field and laboratory instruments, and the development of data on the physical and chemical properties of materials of environmental importance in energy production. This report is one of the Interagency Energy/Environment Research and Development Series reports prepared to provide detailed information on an NBS measurement method or standard development.

C. C. Gravatt, Chief
Office of Environmental Measurements
National Bureau of Standards

ABSTRACT

The development of Standard Reference Materials (SRMs) for aqueous solutions of known concentration of polynuclear aromatic hydrocarbons (PAH) is a high priority but extremely difficult undertaking. This paper is one of a series discussing the development of a "Generator Column" technique for the production of SRMs for PAH's in water. In addition to providing the basis for SRM development, aqueous solubility is a fundamental parameter in assessing the extent and rate of the dissolution of energy based PAHs and their persistence in the aquatic environment. The extent to which aquatic biota are exposed to a toxicant such as a PAH is largely controlled by the aqueous solubility of the toxicant. These solubilities are also of thermodynamic interest, and give information on the nature of these highly non-ideal solutions.

In this study, saturated solutions of individual PAHs were prepared by pumping distilled or salt water through a "Generator Column" maintained at constant temperature. This column was packed with glass beads containing one percent by weight of the PAH compound of interest.

Extraction of the generated PAH solutions was through an "Extractor Column". This column was packed with a superficially porous bonded C_{18} stationary phase (Bondapak C_{18}). This column was found to provide better than 99 percent extraction efficiency for less than 25 ml volumes of aqueous PAH solutions.

After extraction, a water-acetonitrile solvent blend was passed through the "Extractor Column" to elute the adsorbed PAH. This eluate was then passed through a microparticulate analytical column (μBondapak C_{18}) for separation of the PAH from non-analyte interferences. Individual response factors were determined by measuring the UV detector signal produced by injecting a known volume of an acetonitrile solution of the PAH of interest. This report describes the dynamic coupled column liquid chromatographic (DCCLC) procedure. The DCCLC technique was found to be a rapid, accurate, and precise method for measuring PAH aqueous solubilities.

The DCCLC technique was used to obtain solubility data on twelve aromatic hydrocarbons. The aqueous solubility at 25 °C was determined for each compound. The precision of replicate solubility measurements was better than ±two percent. The variation of solubility of each compound with temperature is expressed in the form of either a quadratic or cubic equation on the basis of a least squares fit of the solubility and temperature measurements. These fits have no theoretical significance, but they can be used to interpolate the solubility to within ±two percent of the experimentally measured values between 5 and 30°C. Enthalpies of solution, ΔHs, were then calculated in order to describe the effect of salinity upon solubility. This system was also used to investigate the partitioning of several PAHs between aqueous solutions and sediment samples.

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ACKNOWLEDGMENT

The author is grateful to the U. S. Environmental Protection Agency for partial support of this work under the Interagency Energy/Environment Agreement EPA-IAG-D5-E684. This work is from a dissertation submitted to the Graduate School, University of Maryland, (December 1977) by Willie E. May, in partial fulfillment of the requirements for a Ph.D. degree in Chemistry.

1. INTRODUCTION

The development of a Standard Reference Material (SRM) for aqueous solutions of polynuclear aromatic hydrocarbons (PAH) in a water matrix is an extremely important but difficult undertaking. The need for such SRMs to provide data quality assurance in the measurements and monitoring of energy related organic effluents has been identified in a number of studies, including the series of Workshops sponsored by the National Bureau of Standards and the Environmental Protection Agency, the reports of the Proceedings of which are contained in other publications of this Energy/Environment Series. One of the major SRM recommendations developed by those Workshops was for energy-based PAH in a water matrix. In response, the National Bureau of Standards instituted a project to seek to develop SRMs for PAH's. This report is one of several providing details on the development of that technique, which is based on the "generator column" concept. An understanding of the solubility behavior of PAH's in aqueous systems is imperative before any preparation of SRMs can be performed.

An understanding of the solubility behavior of polycyclic aromatic hydrocarbons (PAHs) in aqueous systems is important in several fields. In water pollution control, such information is helpful in devising abatement processes (1), in modeling natural water systems (2), in designing toxicity experiments, and in developing analytical techniques. In petroleum research, aqueous solubilities are useful in understanding how hydrocarbons might migrate and accumulate to form oil fields (3). In biology, a knowledge of how hydrocarbons behave in water is important for understanding the effects of hydration on the configuration of biopolymers (4). And in chemistry, solubility data are needed for testing models concerned with the behavior of these compounds in aqueous solution (5). For example, Hites (6) has suggested that the natural mechanism that modifies PAH homolog distribution on sediments, following initial deposition, is the differential water solubility of the various alkyl homologs.

The aqueous solubility is a fundamental parameter in assessing the extent and rate of the dissolution of polycyclic aromatic hydrocarbons and their persistence in the aquatic environment. The extent to which aquatic biota are exposed to a toxicant such as a PAH is largely controlled by the aqueous solubility of the toxicant. These solubilities are also of thermodynamic interest, and give information on the nature of these highly non-ideal solutions.

Data on the aqueous solubility of PAHs in the presence of a third component, such as an electrolyte, are also very important. The practical implications are that the presence of this third component may substantially change the solubility, an example being the "salting out effect" of sodium chloride present in seawater (7). Methods for determining PAH aqueous solubilities are subject to errors associated with both the preparation, extraction, and quantitative analysis of saturated solutions. There is

no one method that has addressed the problems associated with each of these processes. Systematic errors associated with quantitative analyses of saturated solutions should be reduced in methods where selective analytical measurement techniques are used. Chromatographic methods allow separation of nonanalyte signals-in-time from those of the analyte. Fluorescence spectroscopy allows greater selectivity than ultraviolet spectroscopy though less than gas or liquid chromatography.

Efficient extraction of saturated aqueous solutions of PAHs with organic solvents is usually not a problem. Problems are however associated with the transfer of aliquots of the saturated solution to extraction vessels. Adsorptive losses of PAHs on the surfaces of transfer tools (pipettes, beakers, etc.) are possible. These errors can be eliminated by rinising the transfer tools with the extracting solvent or by employing methods that do not involve transfer steps.

The source of systematic error that remains, and that is present in all methods that have been used to measure PAH aqueous solubilities, is associated with the preparation of saturated solutions. In all methods that have been reported, saturated solutions were prepared by adding excess quantities of the PAH to water and mechanically mixing the solution for at least 24 hours.

Peake and Hodgson (35, 37) have shown that when hydrocarbons are dissolved by mechanical means, the resulting solutions are often supersaturated. They called this phenomenon accommodation. They showed that accommodated hydrocarbons are not in equilibrium with the water and that their concentrations are a function of hydrocarbon supply, settling time, and mode of introduction.

Wasik and Brown (34) have shown that accommodation is prevented when saturated solutions are prepared by equilibration of hydrocarbon vapors, rather than liquids or crystalline hydrocarbons with water. The methods that employ this approach (33, 34), however, do not have the sensitivity or dynamic range necessary to measure PAH aqueous solubilities accurately.

Although there are values for the aqueous solubility of many PAHs in the literature, they have been reported at only one temperature. The agreement between values determined by different methods is sometimes poor. Furthermore, there have been very few determinations of the aqueous solubility of PAHs in seawater. Because of the increasing need for information about these systems, a study was undertaken to investigate "The Solubility Behavior of Polycyclic Aromatic Hydrocarbons in Aqueous Systems."

In order to begin this investigation, it was necessary to develop a method capable of accurately measuring PAH solubilities. In this method saturated solutions are prepared by an equilibrium process and extracted almost instantaneously. Quantitative analyses of the extract is done by reverse-phase HPLC. Preparation, extraction, and analysis of the saturated solutions all occur within the same system.

In this investigation, this method was used to measure:

(1) The aqueous solubility of some aromatic hydrocarbons;

(2) The effect of temperature on solubility;

(3) The effect of salinity on solubility;

(4) The partitioning of some PAHs between water and sediments.

This methodology is also being used in the development of an aqueous PAH Standard Reference Materials (SRM).

2. SUMMARY AND CONCLUSIONS

The National Bureau of Standards currently issues over 900 Standard Reference Materials (SRM's), with various groups being represented, such as: clinical laboratory standards, trace element standards, nuclear materials, glass viscosity standards, rubber materials, color standards, and coating thickness standards. We are now endeavoring to add to this list an additional group, namely trace organic Standard Reference Materials.

One of the first SRM's from this new group of materials will be an aqueous polynuclear aromatic hydrocarbon (PAH) Standard Reference Material. There are several problems associated with the preparation, storage and handling of aqueous solutions of PAH, that previously prevented the development of this SRM. Now through the use of a dynamic coupled-column liquid chromatographic method developed in this laboratory, we have been able to circumvent these problems. The use of this technique for the preparation and certification of an aqueous PAH SRM will be discussed.

A. Problems Associated with the Preparation and Stabilization of a PAH/Water SRM

Preparation of aqueous PAH solutions of known concentration by gravimetric procedures is difficult because of the extremely low aqueous solubilities of PAH. As shown in Table 9 the aqueous solubilities of many PAH are less than 500 µg/kg (ppb). Preparation of aqueous solutions of known concentration by serial dilutions of a more concentrated organic solution is both hazardous and wasteful. After small aliquots are taken, large volumes of organic solvent containing toxic and expensive chemicals remain to be disposed of.

Preservation of stable aqueous solutions of PAH is hampered by adsorptive losses of the PAH to the surfaces of containers and transfer tools. The magnitude of the adsorptive effect is variable and is a function of the manner in which the solutions are handled. The adsorptive properties of three PAH on four different surfaces are shown in Table 5. These results show that losses of PAH from static solutions to surfaces occur in short periods of time. Stirring such solutions only slightly reduces such losses.

B. Preparation and Quantitation of Dilute PAH Solutions by Dynamic Coupled-Column Liquid Chromatography

Recently, we have developed a dynamic coupled-column liquid chromatographic (DCCLC) method for investigating the aqueous solubility behavior of PAH (39). In the DCCLC method, saturated aqueous solutions of PAH are generated by pumping water through a column packed with glass beads that have been coated with the compound of interest ("generator column"). The concentration of the desired compound in the effluent of the "generator column" is measured by a modification of the coupled-column liquid chromatographic process that has been previously described by May et. al., (38). A flow diagram of this system is shown in Figure 1. Since the aqueous solubility of a compound is a well-defined thermodynamic quantity, saturated aqueous solutions produced by "generator columns" may also be defined as standard solutions at a given temperature.

Stable saturated aqueous solutions are eluted from "generator columns" after an initial aqueous purge volume of approximately 1000 mL. After this initial conditioning, equilibrium is obtained and the PAH concentration at constant temperature has been shown to be independent of flow rate between 0.1 and 5 mL/min. Equilibrium can be re-established after a change in temperature by passing 10 mL of water through the column under the new conditions. A purge volume of only 100 mL is necessary to re-equilibrate a "generator column" after a shelf storage period of as long as three months.

Extraction of the generated PAH solutions is accomplished by passing a measured volume of that solution through an "extractor column" (see Figure 1). This 60 x 0.6 cm column is packed with a superficially porous bonded C_{18} stationary phase (Bondapack C_{18}, Water Associates, Milford, MA) and provides better than 99 percent extraction efficiency for less than 25 mL volumes of aqueous PAH solutions.

After extraction, a water-acetonitrile solvent blend is passed through the "extractor column" to elute the adsorbed PAH. This elute is then passed through a microparticulate analytical column (μBondapak C_{18}) for separation of the PAH from non-analyte interferences. Individual response factors are calculated by replacing the "extractor column" with a calibrated sample loop, and injecting known amounts of the PAH of interest dissolved in acetonitrile.

C. Evaluation of DCCLC as a Method for the Preparation and Certification of an Aqueous PAH SRM

There are several factors that make the DCCLC approach ideal for the preparation and analysis of very dilute aqueous solutions of individual PAH:

1. Saturated solutions are prepared by an equilibrium process. See Section 4, Tables 1 and 2.

2. The use of "generator columns" to produce aqueous PAH solutions circumvents the problems that are usually associated with storing such solutions, since the solutions need not be generated until they are needed.

3. The concentration of the generated aqueous solutions are a function of temperature, and may be expressed in terms of least squares fits of the concentration to temperature. Such equations can be used to interpolate the concentration as a function of temperature to within $\pm$2% of the experimentally determined values between 5 and 30 °C.

4. Both the short and long term precison with which aqueous PAH solutions can be generated appear to be $\leq$2%.

5. Shelf storage of "generator columns" does not seem to present a problem. They have been shown to be stable for longer than 1 1/2 years and through more than 100 liters of aqueous purge.

6. DCCLC is a rapid and accurate method for analyzing the generated dilute aqueous PAH solutions. Analytical errors due to adsorption are minimized in DCCLC because the solution is extracted and concentrated, on line, in less than 500 ms after generation. It has been estimated that this analytical method has an uncertainty of less than 2 percent[2].

3. METHODS FOR MEASUREMENT OF THE AQUEOUS SOLUBILITY OF AROMATIC HYDROCARBONS

The aqueous solubilities of benzene, the alkylbenzenes, and the napthalenes have been measured by several investigators (7-22). All of these investigators prepared saturated solutions by adding an excess quantity of the solute to water and mechanically stirring the mixture for at least twenty four hours. These solutions were usually allowed to settle prior to filtration, extraction, and quantitative analysis by ultraviolet spectroscopy.

This method worked well for the fairly soluble compounds that are being studied. Interlaboratory precision was good. Therefore, this basic methodology, with minor modifications, such as the use of gas chromatography or fluorescence spectroscopy for analysis of the aqueous solutions has been generally adopted for the determination of the aqueous solubilities of PAHs (23-32) even though the solubilities of some PAHs differ from that of benzene by a factor of more than 10^6. In the remainder of this section some of the modifications that have been made on this basic method, and some new approaches to the measurement of the aqueous solubility of aromatic hydrocarbons will be briefly reviewed.

Measurement of Solubility of Nephelometry

In 1942, Davis and co-workers (16) determined the aqueous solubility of 30 PAHs at 29 °C. The solubilities varied from 1600 µg/kg. In this procedure, the test substance was first dissolved in a water miscible solvent such as ethanol or acetone. Dilutions of increasing amounts of this solution with relatively large volumes of water gave a series of turbid suspensions. The turbidity was measured nephelometrically and the relative intensity of scattered light was plotted against the concentration of the test substance. Extrapolation of this standard curve to the relative intensity of a reagent blank gave the experimental solubility.

The precision of replicate analyses was reported to be ±10 percent. The major source of uncertainty was the narrow time frame between saturation of the solution, and coalescence of the dispersed crystals to an extent that would alter the nephelometric behavior of the solution. This approach was also nonselective. It was impossible to discriminate against nonanalyte signals arising from crystalline impurities, dust particles, etc.

Measurement of Solubility by Ultraviolet Spectroscopy

In 1972, Wauchope and Getzen (29) studies the temperature dependence of the aqueous solubility of some PAHs between 25 and 75°C. Saturated solutions were prepared by adding 20 grams of each solid to a 250 mL glass stopped flask containing distilled water. The flasks were suspended in an open water bath and shaken gently for one to three weeks between measurements.

Temperature control was maintained to within ±0.5°C. Samples of the solutions for measurement were withdrawn with pipets through glass wool plugs and emptied into volumetric flasks containing measured amounts of cyclohexane for extraction of the aqueous solutions. The volume of cyclohexane was chosen so that the measured signal fell in the range between 0.5 and 1.5 absorbance units. Although the temperature of the equilibrated aqueous solutions varied from 25 to 75°C, this technique allowed the analyses and the Beer-Lambert coefficient determinations to be performed at room temperature. This method was more selective and it gave better precision (±5%) than the nephelometric method because quantitative analysis was performed at the λ maximum for each individual compound.

Measurement of Solubility by Gas Chromatography

Although this method was not applicable for PAHs, McAuliffe (8) was the first investigator to use chromatography as an analytical tool in the determination of aqueous hydrocarbon solubilities. He measured the solubility of some light alkanes, olefins, and aromatics by making direct 50 µL injections of mechanically-prepared saturated solutions into a gas chromatograph. This chromatographic step allowed him to eliminate (via separation in time) nonanalyte signals contributed by dissolved impurities associated with the analyte. For example, he found that the gas chromatogram of cyclopentane revealed an associated 0.2 percent impurity when injected neat. The size of this impurity peak increased to 25 percent of the size of the cyclopentane peak after euqilibration with water.

Sutton and Calder (9) have also measured the solubilities of several alkylbenzenes in distilled water and in sea water by a method based on gas chromatography. Saturated solutions were prepared by equilibrating water with aromatic vapor in an all-glass apparatus consistine of a one-liter Erlenmeyer flask with an insert tube. The insert tube was used to store the compound. It was capped with a ground-glass stopper. The liquid hydrocarbon did not come into contact with the water except through a perforation in the insert, which allowed hydrocarbon vapors to enter the headspace above the water in the flask. The flask was placed in a constant temperature-shaking bath controlled at 25.0 ± 0.1°C. The water was equilibrated for 48 hours prior to analysis. The solubilities were determined by solvent extraction of the saturated solutions with subsequent analyses of the extracts by gas chromatography.

The solubilities reported by Sutton and Calder were 5 to 20 percent higher than those determined by McAuliffe. This is not surprising since the McAuliffe method is susceptible to serious losses due to adsorption of the hydrocarbons on the walls of the syringe. (See Section 3, pages 16-18, for a discussion of the phenomenon.) Sutton and Calder injected concentrated organic extracts rather than dilute aqueous solutions. This reduced the chances for adsorptive losses during injection and increased the sensitivity of the method. However, neither McAuliffe's nor Sutton and Calder's method is sufficiently sensitive for determination of the aqueous solubility of PAHs.

Determination of Solubility by Headspace Analysis

Some researchers have determined the aqueous solubility of several benzenes and naphthalenes using a headspace analysis method. In 1971, McAuliffe (33) reported hydrocarbon solubilities determined by the following method. A 50 mL glass hypodermic syringe was filled with equal volumes of an aqueous hydrocarbon solution and helium. The mixture was vigorously agitated for 20 minutes on a wrist-action shaker to establish equilibrium between the phases. The gas phase was then flushed through a sample loop of a gas sampling valve and injected into a gas chromatograph. A fresh supply of helium was added to the syringe and equilibrated with the aqueous solution and treated as before. A plot of log peak area in the gas phase versus equilibration number (gas volume) produced a straight line. The parition coefficient (ClCg) between the gas and liquid phase can then be calculated from the slope of the plot and the gas and liquid volumes. The solubility is the product of the partition coefficient and the saturated vapor pressure.

Wasik and Brown later (34) modified McAuliffe's static headspace method. They constructed a dynamic headspace analysis unit where hydrocarbons were introduced into the apparatus as vapors to avoid the danger of emulsion formation (35), which can occur when liquid hydrocarbons are mixed with water. They allowed the gas mixtures to circulate through the liquid phase for at least 1/2 hour to insure that equilibrium was attained. After the first equilibration, a small portion of the headspace was sampled via a gas sampling valve and measured by gas chromatography, while the remainder was vented to waste. Fresh helium was then added, equilibrated with the aqueous solution and analyzed as before. The partition coefficients were calculated as in McAuliffe's method.

Determination of solubility by headpsace analysis offers several advantages over spectrophotometric techniques. First, because of the selectivity of chromatographic analysis, compound purity is not a critical factor; second, absolute calibration of the gas chromatographic detector is not necessary if the response is linearly related with concentration over the range necessary for the measurements; and finally, this method does not require the preparation of saturated solutions, since a partition coefficient, not a solubility, is actually measured. However, headspace methodology would probably not be applicable for determining PAH solubilities for three reasons. First, there is little data in the literature on the vapor pressures of PAHs. Second, the aqueous solubilities of most PAHs are too low to be measured by this procedure. Finally, adsorptive losses of PAHs to glass surfaces from the vapor phase would cause errors.

Measurement of Solubility by Fluorescence Spectroscopy

Recently, Schwarz (31) has measured the temperature dependence of the solubilities of several PAHs in aqueous solutions by a fluorescence method. Saturated solutions were prepared and measured *in situ* in modified fluorescence cells. Each cell contained 5 ml of an aqueous

solvent with an excess amount of the PAH to be studied. The cells were rotated for at least 24 hours at each temperature before the solution was allowed to settle and be measured. The fluorescent intensity of these saturated aqueous PAH solutions was found to be proportional to concentration between 8 and 30°C. The fluorescence measurements were put on an absolute scale by ultraviolet spectroscopic (UV) measurements at 25°C.

This fluorescence method has two major advantages over the methods previously described for measuring the solubilities of PAHs in aqueous solutions. First, no transfers of the saturated solutions are made so that systematic errors arising from adsorption on the transfer tools is eliminated. Fluorescence is also inherently more selective for PAHs than UV and other nonluminescence spectroscopic techniques. Nonanalyte signals may be reduced through both selective excitation and selective monitoring of fluorescence (emission). This latter advantage is partially negated, however, since the absolute measurement is made by UV. One of the disadvantages of the method lies in the fact that the solutions cannot be filtered prior to analysis to remove suspended microcrystals and other particulate matter.

Estimations of Solubility by High Performance Liquid Chromatography

Locke (36) has used a reverse-phase high performance liquid chromatographic (HPLC) method to estimate the aqueous solubilities of some PAHs. He made the following postulates: selectivity in reverse-phase HPLC is governed by the solubilities of similar solutes in the mobile phase; group selectivity is determined by both the stationary and mobile phases; selectivity toward individual components within a group is set by the eluent. The eluent used in reverse-phase HPLC is a blend of water and an organic solvent that is miscible with water. Acetonitrile or methanol is most often used as the organic component. PAHs (up to 5 condensed rings) are fairly soluble in both acetonitrile and methanol. The aqueous solubilities of PAHs are low and vary between 1 and 2000 µg/kg. Selectivity then is based on the differences in the aqueous solubility of the individual PAHs. Locke suggested that a linear relationship should exist between log retnetion volume and log solubility of unsubstituted PAHs. He used the solubilities of benzene and fluoranthene to define the slope of the line, and determined the solubilities of other aromatic hydrocarbons from this relationship.

Locke's method provides a rapid and simple means for estimating the aqueous solubilities of PAHs. Individual solubility values can be estimated to within 200 percent. However, these extrapolated values differ too greatly from measured solubilities for this procedure to be categorized as a valid method of determining the aqueous solubility of PAHs.

4. EXPERIMENTAL PROCEDURES

DEVELOPMENT OF DYNAMIC COUPLED COLUMN LIQUID CHROMATOGRAPHY - AN ACCURATE METHOD FOR THE DETERMINATIONS OF THE AQUEOUS SOLUBILITY OF POLYNUCLEAR AROMATIC HYDROCARBONS

Any method for determining the aqueous solubilities of PAHs must provide a means of preparing saturated solutions of the compounds of interest, and performing quantitative analysis of those solutions. Some of the methods previously reported in the literature for determining PAH aqueous solubilities were reviewed in Section 1. The accuracy and precision of these methods can be adversely affected by a number of processes including: incomplete equilibration of the solid hydrocarbons with the aqueous medium; dispersion rather than true dissolution of the solid hydrocarbons (accommodation); failure to remove suspended microcrystals from the solution; losses of the PAHs from solution to the surfaces of containers, filters and transfer tools due to adsorption.

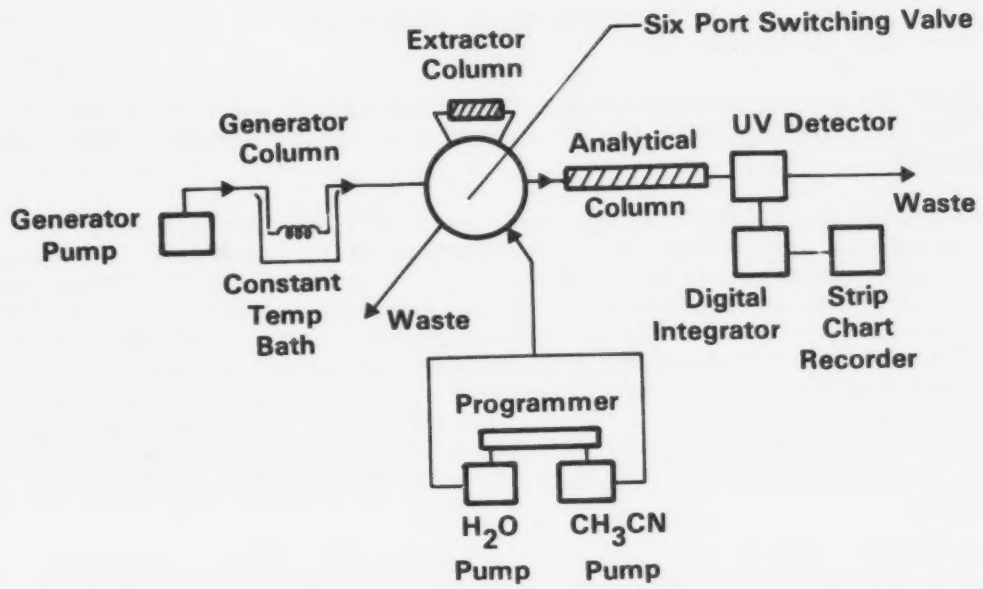
The dynamic coupled column liquid chromatographic (DCCLC) technique which will be discussed in this section circumvents all the problems started above. In addition to a description of this technique this section includes a critical evaluation of the method in terms of the saturated solution preparation, transfer, extraction, and quantitative analysis processes. The section is concluded with a discussion of the precision and potential accuracy of this method.

Methodology

This method for determining aqueous solubility is based on generating saturated solutions by flowing water through a column packed with glass beads coated with the compound to be measured (generator column). The concentration of the desired compound in the effluent from the generator column is measured by a modification of the coupled column liquid chromatographic procedure developed by May et al. (38). A flow diagram of the system is shown in Figure 1.

Reagents--

The water used in this study was distilled from a potassium permanganate-sodium hydroxide solution and passed through an XAD-2 column (38). The acetonitrile and sodium chloride were spectro and reagent grades, respectively. All of the PAHs used were obtained commercially and were reported to contain



Detail of Six Port Switching Valve

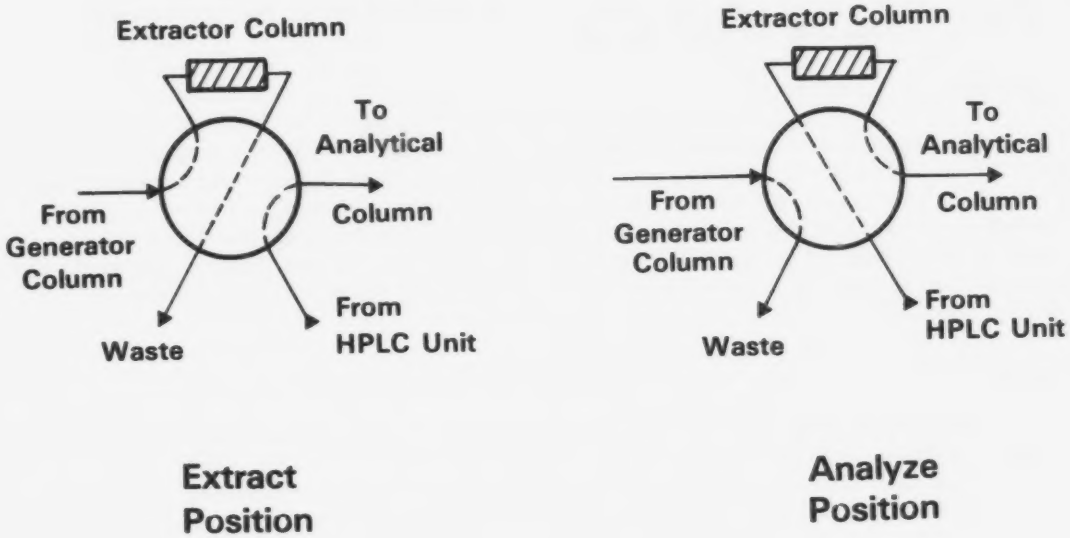


Figure 1. Dynamic coupled column liquid chromatographic flow diagram.

less than three percent impurities by their respective manufacturers. Gas and liquid chromatographic analyses of these materials supported these claims.

Preparation of Saturated Solutions Using "Generator Columns"--

Columns for the generation of saturated solutions of PAHs were prepared by packing 60 x 0.6 cm stainless steel columns with 60-80 mesh glass beads coated with 1 percent (wt/wt) of the compound of interest. The beads were coated by adding 20 grams of the beads to 200 ml of a 0.1 percent methylene chloride solution of the PAH of interest and stripping the solvent with a rotary evaporator.

Columns for the generation of saturated solutions of liquid aromatic hydrocarbons such as benzene were prepared by pumping 50 mL of the liquid through a 60 x 0.6 cm stainless steel column with uncoated glass beads. Excess amounts of benzene were purged from these columns with 50 mL of water.

Saturated solutions were generated by pumping distilled water or saline solutions through these columns at flow rates ranging between 0.1 and 5 mL/min. These columns were thermostated by means of a water bath controlled to ±0.05 °C.

Extraction of Generated Solutions--

Extraction of the PAHs from the generated solutions was accomplished by flowing a measured volume of the solution through a 6 x 0.6 cm stainless steel "extractor column" packed with a 37-50 μm superficially porous support with a bonded C18 stationary phase (Bondapak C18, Waters Associates, Milford, MA) and fitted on both ends with 2 μm frits. This column has been found to provide greater than 98 percent extraction efficiency for less than 25 ml volumes of aqueous PAH solutions. (See Appendix A-1) Generated solutions of benzene were not passed through the "extractor column", but were injected directly into the chromatographic system via a loop sample injector. Reasons for this modification are discussed later in the section and in Appendix A-1.

Chromatographic Transfer and Analysis of Extract--

After extraction, flow from the "generator column" was diverted to waste, while an acetonitrile - water solvent blend from a HPLC gradient pumping system (Waters, Associates, Milford, MA) was simultaneously routed through the "extractor column" to elute the adsorbed compounds. The eluate then passed through a 30 x 0.6 cm microparticulate analytical column (μBondapak C18, Waters Associates) for separation of individual PAHs from nonanalyte interferences such as those caused by crystalline impurities. Isocratic elution conditions were usually employed, resulting in some band broadening in the transfer of extracted components from the extractor to the analytical column. The band broadening resulting from this transfer process was eliminated when necessary by employing a linear solvent gradient from water to acetonitrile. This caused elution focusing of the components at the head of the analytical column. A detailed discussion of this phenomenon is given elsewhere (39).

The integrated UV detector signal produced by each of the aromatic hydrocarbons was determined to be proportional to its concentration. Individual response factors were found for each compound by first replacing the "extractor column" with a calibrated sample loop and then injecting acetonitrile solutions with known concentration of the individual hydrocarbons. Details concerning the loop calibration technique and preparation of the acetonitrile solutions are given in Appendices A-3 and A-4 respectively.

Critical Evaluation of the DCCLC Method

The development of an accurate method for determining the aqueous solubility of PAHs is contingent upon the ability of that method to prepare, maintain, transfer and analyze saturated solutions. In this section some of the problems associated with PAH solubility methodology in general are discussed along with explanations of how these problems are circumvented by the DCCLC approach.

Production of Saturated Solutions Via an Equilibrium Process--

Stable saturated solutions were eluted from generator columns after an initial aqueous purge volume of between 100 and 500 mL. After this initial conditioning, equilbrium was obtained and the PAH concentration at constant temperature became independent of flow rate between 0.1 and 5 mL/min (see Table 1). Equilibrium could be re-established after a change in temperature or salinity by passing 10 mL of water through the column under the new conditions. A purge volume of approximately 50 mL was necessary to recondition a "generator column" after a shelf storage period of three months.

TABLE 1. PHENANTHRENE SOLUBILITY DEPENDENCE ON THE AQUEOUS FLOW RATE THROUGH A "GENERATOR COLUMN"

Flow Rate (mL/min.)	Concentration[a] (µg/kg)
5.0	865±7
0.4	868±4
0.1	866±3
Temperature	22.0 °C

[a]The concentration reported represent the averages of five measurements at each temperature. The uncertainties represent the standard deviation of the mean at each temperature.

The reversible nature of this process was demonstrated by the following experiment. Distilled water was pumped through two independently thermostated generator columns that were connected in series. The temperature of the first column, "A", was maintained at 24.3 °C. Concentration measurements were made on the effluent from the second column in the series, "B", at temperatures of 25.3, 12.8 and 6.6 °C. The concentration of the solution that eluted from column "B" of the series, at each temperature, was identical, within experimental error, to the concentration that had been obtained from column "B" alone. The data from this experiment is presented in Table 2.

TABLE 2. A DEMONSTRATION OF THE EQUILIBRIUM-REVERSIBLE NATURE OF THE SOLUTION GENERATING PROCESS WITH "GENERATOR COLUMNS"

Generator Column "A"		Generator Column "B"		Generator Column "A" + "B" in series	
Temp (°C)	Conc. (µg/kg)	Temp (°C)	Conc. (µg/kg)	Temp (°C)	Conc. (µg/kg)
24.3	42.7	25.3	45.5±0.2	25.3	45.4±0.1
		12.8	21.3±0.2	12.8	20.7±0.1
		6.6	14.0±0.1	6.6	14.2±0.2

The flow rate through these anthracene "Generator Columns" was 5.0 mL/min.

Normally saturated PAH solutions were generated by pumping distilled water through "generator columns". The results of this experiment show that identical results were obtained when the opposite situation was imposed, that is the PAH concentration in the feed solution was greater than that expected in the effluent. This could only happen through an equilibrium process.

Accommodation--

It is well established that hydrocarbons can exist in colloidal, micellar or particulate form in appreciable quantities. This was first noted by Peake and Hodgson (35,37) who found that filtration reduced the apparent solubility or "accommodation" measured for hydrocarbon solutions prepared by mechanical means. They also found that the degree of accommodation (difference between the measured and equilibrium amounts of hydrocarbons in the water) was a function of hydrocarbon supply, settling time, filtration pore size, and the mode by which crystalline hydrocarbons were introduced into the solutions.

The saturated solutions produced by "generator columns" are independent of hydrocarbon supply. Phenanthrene solutions of identical concentrations were generated by a "generator column" prepared by the procedure described earlier (coated glass beads) and one prepared by packing a 60 x 0.6 cm column with crystals of phenanthrene (see Table 3). The concentrations of the solutions produced by "generator columns" are also stable through large volumes of aqueous purge, where the supply of hydrocarbon on the column is being steadily depleted (see Table 8). This depletion however represents only a small percentage of the total amount of compound on the column.

TABLE 3. SOLUBILITY DEPENDENCE ON THE SUPPLY OF PHENANTHRENE ON A "GENERATOR COLUMN"

1% Phenanthrene on Glass Beads Column (60 x 0.6 cm)		Crystalline Phenanthrene Column (60 x 0.6 cm)
Phenanthrene Concentration in Generator Column Effluent		
(µg/kg)		(µg/kg)
959		938
947		935
958		943
955±7	Average	939±4

Aqueous Flow Rate - 5 mL/min.

Temperature - 24.3 °C

Differential settling times are not a problem because the saturated solutions are generated and measured almost instantaneously, all within the same system.

Filtration of the saturated solutions does not alter the concentration of the solutions generated by "generator columns" because the solutions are actually filtered during, and not after preparation. The filters (snubbers) which are fitted on both ends of these columns are saturated with the PAH of interest during the initial column conditioning period and are therefore an integral part of the solution generating system.

Nonanalyte Signals--

One of the problems that reduces the accuracy of methods that use spectroscopic techniques for the measurement of solubility is the presence of

dissolved impurities which contribute to the spectroscopic signal. The most direct method for eliminating this problem is by the use of ultrapure chemicals. Ultrapure PAHs, however, are difficult to obtain. Thus selective analytical techniques must be used to minimize such interferences.

The method discussed in this report employs a reverse phase liquid chromatographic procedure which separates the signals produced by nonanalyte constituents, in time, from the signal produced by the analyte. The use of this technique can also relax the purity requirements for the individual PAHs. The following experiment was performed to illustrate this point: A generator column coated with a 1 percent blend of a 90 percent 2-methylantracene, 7 percent phenanthrene, and 3 percent of several other PAHs was prepared, conditioned and purged with 4500 ml of water at 25.4 °C. The results of this experiment are presented numerically in Table 4 and graphically in Figure 2. It should be noted that impurities are eluted from the column along with the analyte. After initial conditioning, the concentration of the 2-methylanthracene is stable while the concentrations of the impurities continue to diminish. The measured concentration of 2-methylanthracene produced by the impurity containing column at 25.4 °C was 21.8±0.4 µg/kg. The concentration of the solution produced by a "generator column" packed with glass beads coated with only 2-methylanthracene and run under identical conditions was 22.6±0.5 µg/kg.

TABLE 4. EFFECT OF AN ADDED IMPURITY, PHENANTHRENE, ON THE CONCENTRATION OF 2-METHYLANTHRACENE SOLUTION GENERATED AT 25.4 °C

Volume Pumped Through "Generator Column" (mL)	Phenanthrene Conc. (µg/kg)	2-Methylanthracene Conc. (µg/kg)
0	<1215	21.6
75	1215	21.6
225	1219	22.3
375	1198	21.4
525	1194	22.1
675	1196	22.8
825	1193	21.8
975	1183	21.9
4500	161	21.7

Note: Measured 2-Methylanthracene concentration - 21.8±0.4 µg/kg. Concentration calculated from a least square fit of solubility and temperature data obtained using a "generator column" packed with 99% pure 2-Methylanthracene - 21.9±0.2 µg/kg.

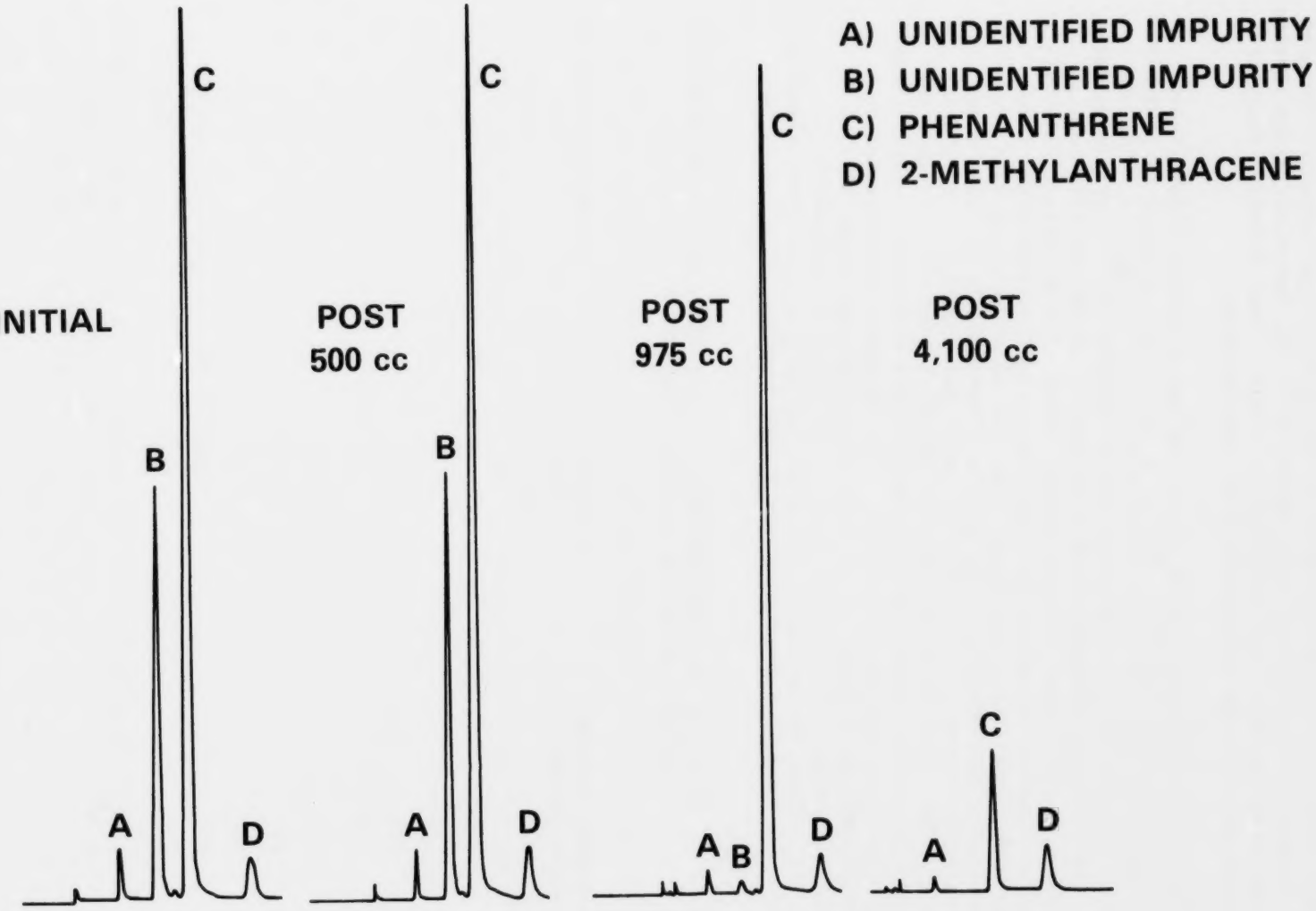


Figure 2. Effect of impurities on analyte solubility measurement.

Adsorption--

The most elusive analytical interference associated with the measurement of PAH aqueous solubilities is that of adsorptive losses of these compounds from solution to the surfaces of containers and transfer tools. PAH adsorption causes reductions in the measure analyte signal, whereas the other interferences discussed up to this point cause positive errors.

The magnitude of the adsorption effect is variable and a function of the manner in which the solutions are handled. The adsorptive properties of three PAHs on four different surfaces are shown in Table 5. These results show that losses of PAHs from static solutions to surfaces occur in short periods of time. The use of caffeine as a PAH complexing agent (32) reduces these losses, but does not eliminate them (see Table 6). Stirring the solutions causes only small reductions in these losses. The PAH losses shown in Table 6 for stirred solutions are less than those reported in Table 5 for static solutions.

TABLE 5. SURFACE ADSORPTION CHARACTERISTICS OF PAHs AQUEOUS SOLUTIONS[a]

	Percent Loss from Solution					
	Phenanthrene		Chrysene		Benz(a)Pyrene	
	1 Hr	13 Hrs	1 Hr	13 Hrs	1 Hr	13 Hrs
Glass	8		46	71	53	82
Silanized Glass	5	73	64	81	73	93
Platinum	35	87	66	85	57	93
Aluminum	5	76	50	89	67	95

[a]The concentration of each PAH was 1 µg/kg.

Surface to volume ratios are approximately equal to approximately 1 cm^2/cm^3 for all materials studies. All measurements are made by the coupled column LC technique described by May et al. in Reference 38.

The dynamic coupled column liquid chromatographic system was also designed to circumvent problems due to adsorption. After preparation and filtration, saturated solutions are transferred and extracted by a process that minimizes PAH contact with surfaces. The volume between the "generator column" and the "extractor column" is approximately 6 µL. The time required for transfer of the saturated solutions at a flow rate of 5 mL/min is less than 75 micro-seconds. Furthermore, the walls of the transfer lines are pre-saturated with the compound being studied during the column conditioning process. This further reduces the possibility of adsorptive losses of the PAHs during the brief time that the saturated solutions remain in these lines.

TABLE 6. LOSSES OF VARIOUS PAHS FROM AQUEOUS SOLUTIONS CONTAINING CAFFEINE AS A COMPLEXING AGENT[a]

Experiment	Complexing Agent	Experimental Conditions	Percent Loss			
			Pyrene	Chrysene	3,4 Benzpyrene	1,2,5,6-Dibenzanthracene
1	0.1% Caffeine	Stir 4 hr, then analyze	10	10	10	44
	None	Stir 4 hr, then analyze	29	61	68	78
2	0.1% Caffeine	Stir 16-20 hr, then analyze	25	29	32	61
	None	Stir 16-20 hr, then analyze	74	72	86	85
3	0.1% Caffeine	Stir 40 hr, then analyze	12	22	25	61
	None	Stir 40 hr, then analyze	96	93	96	97

[a]0.5 µg of each PAH present in 500 mL of distilled water (1 µg/kg per compound).

Direct injection of the generated saturated solutions into the chromatographic system via a sample loop was initially attempted. PAH adsorptive effects, however, restricted the use of this more simple and rapid measurement approach to only relatively soluble aromatic hydrocarbons such as benzene (solubility 1800 ppm at 25 °C). The results presented in Tables 5 and 6 indicate that the magnitude of the adsorption problem is inversely related to aqueous solubility. Therefore, substitution of a stainless steel sample loop for the "extraction column" would be expected to cause systematic positive errors. The results presented in Table 7 indicate that the size of these errors would be a function of both the solubility of the hydrocarbon and the volume of saturated solution passed through the loop prior to injection into the chromatographic system. The data presented in Table 7 also shows that adsorptive errors may be eliminated from the aqueous solubility determination of benzene by limiting the volume of saturated solution passed through the loop to 50 µL prior to injection (one stroke of the pump used to pass water through the generator column delivers 50 µL). The magnitude of the errors caused by adsorption on the walls of the sample loop were much greater for naphthalene (see Figure B-2 in Appendix B) and the less soluble PAHs, and were not eliminated by limiting the volume of saturated solution passed through the loop to 50 µL prior to injection. Because of these adsorptive errors, saturated solutions of all the compounds studied in this investigation, with the exception of benzene, were extracted via an "extraction column" and transferred to the chromatographic system via the coupled-column process that was described in this section.

The Potential Accuracy of the DCCLC Method--

The preparation of saturated solutions by "generator columns" has been shown to be the result of an equilibrium process. It has been demonstrated that the "extractor column" can provide quantitative extraction of naphthalene and the PAHs from aqueous solutions. Problems associated with the stability of aqueous PAH solutions are avoided because the solutions are instantaneously analyzed after they are generated. Nonanalyte signals are separated from those of the analyte by chromatographic means. The potential accuracy of the DCCLC method is then limited by the liquid chromatographic analysis of the generated PAH solutions.

The accuracy of the liquid chromatographic analysis of the generated solutions is limited by the uncertainties involved with the calibration of the sample loop, preparation of standard acetonitrile solutions of the PAHs and the volumetric measurement of the amount of saturated solution sampled for a given analysis. The random errors that are associated with each of these processes have been estimated to be less than ±1.2 percent, ±0.1 percent, and ±1.0 percent, respectively. An explanation of how each of these estimates was made is presented in Appendix A. Quadratic addition of these random errors yields a minimum uncertainty of 1.6 percent for the quantitative analysis of the generated saturated solutions and hence a potential accuracy of greater than 98 percent for the method.

TABLE 7. ADSORPTION OF SOME AROMATIC HYDROCARBONS FROM AQUEOUS SOLUTION TO STAINLESS STEEL SAMPLE LOOP[a] AT 25 °C.

Volume of Saturated Solution Passed Through Loop (mL)	Apparent Concentration (mg/kg)
Benzene	
.05	1795
1.00	1800
10	2273
25	2728
Naphthalene	
.05	32.0
0.20	32.2
2.0	35.0
5.0	36.4
10	37.8
Phenanthrene	
.05	0.97
4.0	1.36
9.2	1.61
11.0	1.70

The concentrations of these generated solutions as determined by solvent extraction followed Liquid Chromatographic analysis (Benzene) of DCCLC were:

Benzene - 1800 ±50 (mg/kg)
Naphthalene - 31.8 ±1
Phenanthrene - 0.95± .02

[a]Sample Loop Volume - 23.1 µL

Generator Column
Flow Rate - 0.4 mL/min. in all cases.

Reproducibility--

Both the short and long term precision with which saturated solutions can be generated and measured are better than ±3 percent. The results presented in Table 8 demonstrate this fact.

TABLE 8. PRECISION WITH WHICH ANTHRACENE SOLUTIONS MAY BE GENERATED AND MEASURED AT 25.4 °C

Volume of Distilled Water Eluted Through Column (mL)	Concentration Measured (µg/kg)
1	45.2
190	47.0
230	46.6
500	46.1
775	46.9
910	44.6
1175	45.5

Average Measured Concentration (6-21-77) - 46.0±0.9

Concentration Calculated from Calibration Curve (12-20-76) - 45.7

Concentration Measured by Solvent Extraction Followed By GC Analysis (6-21-77) - 45.8±1.0

THE APPLICATION OF DYNAMIC COUPLED COLUMN LIQUID CHROMATOGRAPHY TO THE DETERMINATION OF THE AQUEOUS SOLUBILITY AND OTHER RELATED PARAMETERS OF SOME AROMATIC HYDROCARBONS

Aqueous solubility data for the twelve aromatic hydrocarbons studied in this investigation are reported in this section. The solubilities determined spanned a range of 10^6. The solubilities measured at 25 °C are compared

to values reported by other investigators and are correlated with molecular parameters such as carbon number, molar volume and molecular length.

The variations of solubility with both temperature and salinity are reported. Enthalpies of Solution, ΔHs, are calculated from the temperature dependence of the solubility, and the effect of salinity on solubility, expressed in terms of the Setschenow constant, is reported for each compound.

Aqueous Solubilities at 25 °C

Table 9 compares the solubilities determined by DCCLC with some values reported by other investigators. Of the twelve values reported, there are only two cases of gross disagreement with the consensus literature value. Those are the values for anthracene and triphenylene.

The solubilities reported for anthracene are clustered about two values. A possible reason for this phenomenon lies in the fact that most commercial preparations of anthracene contain at least two percent phenanthrene. Though the two compounds are structural isomers, phenanthrene is approximately twenty times more water soluble than anthracene. The presence of phenanthrene in solution would contribute a positive systematic error to methods that employ nonspecific analytical measurement techniques, such as ultraviolet spectroscopy (29) and nephelometry (24). The value reported by Schwarz (31), who employed a more selective analytical technique (fluorescence) agrees with that determined by DCCLC.

The aqueous solubility of triphenylene as determined by DCCLC is in gross disagreement with all other literature values. The reason for this discrepancy is unknown. DCCLC values obtained through use of triphenylene prepared by different commercial manufacturers were identical. Neither variations in the length of, nor triphenylene supply on, the "generator column" had any effect on the solubility determined.

Variation of Solubility with Temperature

Solubility data for benzene, naphthalene and ten other PAHs are presented in Table 10 in the form of either a quadratic or cubic least squares fit of the solubility to temperature for each compound. These fits have no theoretical significance, but can be used to interpolate the solubility as a function of temperature to within ±2 percent of the experimentally measured values between 5 and 30 °C. The experimental values from which these equations were derived are given in Appendix B.

The data presented in Appendix B-1 show that the DCCLC method has both sufficient precision and accuracy to detect a minimum in solubility profile of benzene in the region between 17.5 and 18.0 °C although the solubility never varies by more than 2.5 percent between 5 and 25 °C. This effect has been previously observed and reported by several other investigators (10,11,16,34).

TABLE 9. THE AQUEOUS SOLUBILITIES OF SOME AROMATIC HYDROCARBONS AS DETERMINED BY SEVERAL INVESTIGATORS

Compound	Molecular Weight	Solubilities (mg/kg)						
		This Work		Davis[a]	MacKay[b] & Shui	Schwarz[c]	Wauchope[d] & Getzen	
		25 °C	29 °C	29 °C (1942)	25 °C (1977)	25 °C (1977)	(1972)	Others
Benzene	78.1	1791 ± 10						1780(34),1796(22), 1755(13),1780(12)
Naphthalene	128.2	31.69 ± .23			31.7 ± .2	30.3 ± .3	31.2	34.4(11)
Fluorene	166.2	1.685 ± .005			1.98 ± .04		1.90	
Anthracene	178.2	.0446 ± .0002	.0570 ± .003	.075 ± .005	.073 ± .005	.041 ± .0003	.075	.075(28,30)
Phenanthrene	178.2	1.002 ± .011	1.220 ± .013	1.600 ± .050	1.290 ± .070	1.151 ± .015	1.180	.994(32)
2-Methylanthracene	192.3	.0213 ± .003						
1-Methylphenanthrene	192.3	.269 ± .003						
Fluoranthene	202.3	.206 ± .002	.264 ± .002	.240 ± .020	.260 ± .020		0.265	0.240(32)
Pyrene	202.3	.132 ± .001	.162 ± .001	.165 ± .007	.135 ± .005	.129 ± .002	.148	
1,2-Benzanthracene	228.3	.0094 ± .0001	.0122 ± .0001	.011 ± .001	.014 ± .0002			.010(28)
Chrysene	228.3	.0018 ± .00002	.0022 ± .00003	.0015 ± .0004	.002 ± .0002			.006(28)
Triphenylene	228.3	.0066 ± .0001		.038 ± .005	.043 ± .001			.043(28)

[a] Solubilities determined by the nepholometric method described in Reference (24).

[b] Solubilities determined by method described in Reference (26).

[c] Solubilities determined by fluorimetric method described in Reference (31).

[d] Solubilities determined by UV method described in Reference (29).

TABLE 10. VARIATION OF AQUEOUS SOLUBILITY WITH TEMPERATURE

Compound	Solubility Dependence on Temperature ($\mu g/kg$)[a]	Correlation Coefficient[a]
Benzene	$(0.0247t^3 - 0.6834t^2 + 0.3166t + 1833) \times 10^3$	.9443
Naphthalene	$(0.0189t^2 + 0.2499t + 13.66) \times 10^3$	.9987
Fluorene	$0.0185t^3 + 0.4543t^2 + 22.76t + 543$	.9999
Phenanthrene	$0.0025t^3 + 0.8059t^2 + 5.413t + 324$	.9992
1-Methylphenanthrene	$0.0080t^3 - 0.1301t^2 + 6.802t + 55.4$	.9994
Pyrene	$-0.0011t^3 + 0.2007t^2 - 1.051t + 50.2$	.9997
Fluoranthene	$0.0072t^3 - 0.1047t^2 + 4.322t + 50.4$	.9988
Anthracene	$0.0013t^3 - 0.0097t^2 + 0.8861t + 8.21$	.9998
2-Methylanthracene	$0.0011t^3 - 0.0306t^2 + 0.8180t + 2.79$	.9988
1,2 Benzanthracene	$0.0003t^3 - 0.0031t^2 + 0.1897t + 1.74$	.9991
Chrysene	$0.0024t^2 + 0.0144t + 0.609$	.9982
Thiphenylene	$-0.002t^3 + 0.0250t^2 - 0.4250t + 4.89$	.9990

[a]These equations and correlation coefficients were obtained by fitting solubility vs. temperature data to a Polynomial Regression (2° or 3°) program supplied with a Hewlett Packard 9830A Calculator.

Calculation of the Enthalpy of Solution

The solubility data presented in the preceding section can be used to calculate the heat of solution, ΔH_s, from the following relationship:

$$d(\ln S)/_{d(1/T)} = -\Delta H_{s/R} \quad (1)$$

where T is the absolute temperature, R is the ideal gas constant, and S is the molar solubility at T. Values of ΔH_s at 298 °K were calculated from a least squares fit of the integrated form of equation (1), namely

$$\ln S = -\Delta H_s/RT + b, \text{ where b is a constant.} \quad (2)$$

The results of these least squares fits are presented graphically in Figure 3. Values of ΔH_s for eleven of the compounds studied in this investigation are found in Table 11 along with values for ΔH_s determined by other investigators. A single value of ΔH_s cannot be reported for benzene because the enthalpy of solution varies with temperature.

TABLE 11. ENTHALPIES OF SOLUTION OF SOME AROMATIC COMPOUNDS BETWEEN 5 AND 30 °C

	Enthalpy of Solution (Kcal/Mol)		
Compound	This Work	Schwarz[a]	Wauchope[b] & Getzen
Naphthalene	6.30 ± .12	5.29 ± .10	6.10 ± .28
Fluorene	7.88 ± .15		6.99 ± .16
Anthracene	10.46 ± .10	8.32 ± .38	10.4 ± .8
Phenanthrene	8.32 ± .14	8.68 ± .23	7.7 ± .9
1-Methylphenanthrene	9.34 ± .18		
2-Methylanthracene	10.10 ± .17		
Fluoranthrene	9.52 ± .38		
Pyrene	8.47 ± .36	11.4 ± .2	7.3 ± .2
1,2-Benzanthracene	10.71 ± .25		
Chrysene	9.86 ± .24		
Triphenylene	10.71 ± .39		

[a] Reported in reference 31.

[b] Calculated from solubility data reported in Reference 29 in the 0-30° temp. range.

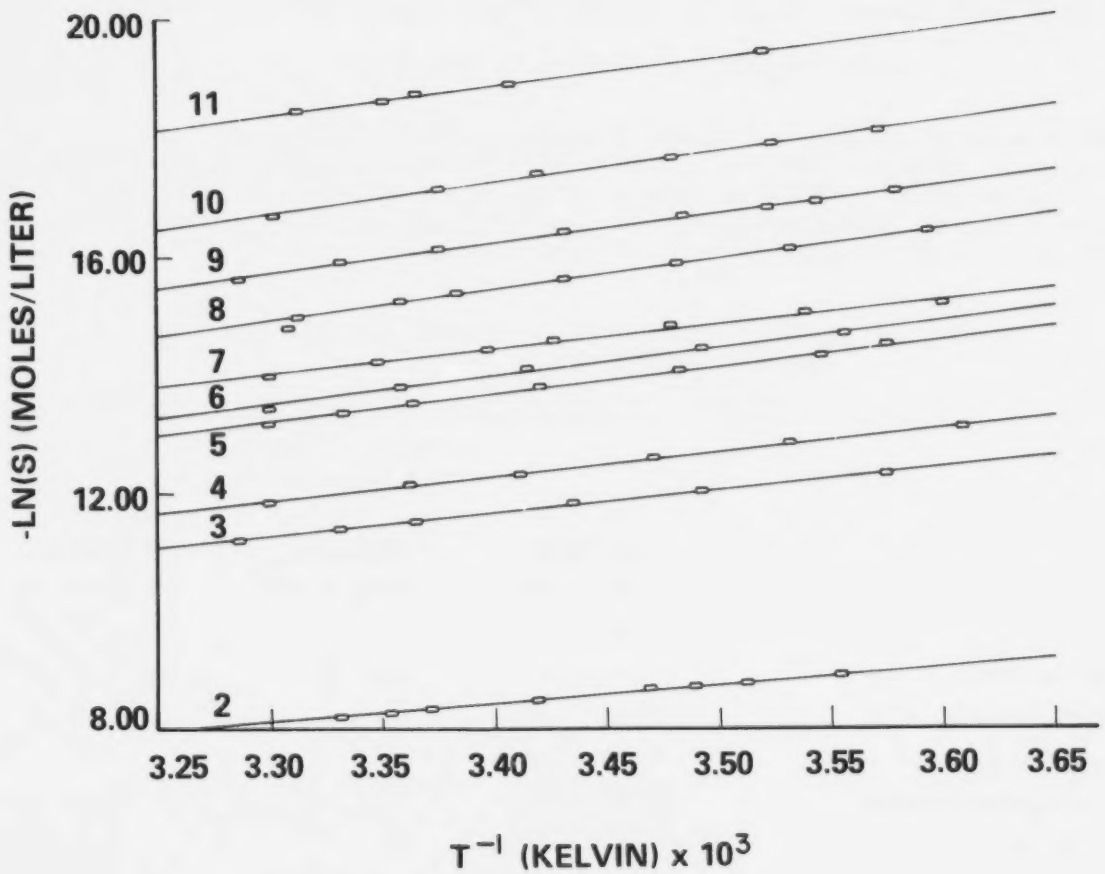


Figure 3. The dependence of the solubility of some PAHs on temperature.

Variation of Solubility with Salinity

Determination of the solubility of PAHs in water is of both thermodynamic interest and of practical relevance in assessing the environmental fate and effects of oil present in rivers, lakes, ground water, and oceans. Although the aqueous solubilities of a large number of specific PAHs have been measured and correlated, few data exist on the solubility in the presence of a third component such as an electrolyte. The practical implications are that the presence of this third compound may substantially change the solubility, an example being the "salting out" effect of sodium chloride present in sea water.

Setschenow (40) derived an empirical relationship for the magnitude of the "salting out" effect, that is, the dependence of solubility on the salt concentration of saline solutions:

$$\log So/Ss = K_s C_s$$

where So and Ss are the concentrations of the solute in fresh and salt water, respectively, K_s is the Setschenow constant for the sodium chloride solution and C_s is the molar salt concentration. The solubility of phenanthrene as a function of ionic strength and temperature is illustrated graphically in Figure 4. The value of the Setschenow constant is shown to be independent of temperature over the range studied. The Setschenow constants calculated in the same fashion for the compounds studied in this investigation are presented in Table 12.

TABLE 12. SETSCHENOW CONSTANTS FOR SOME AROMATIC HYDROCARBONS AT 25 °C

Compound	K_s (liters/mole)	
Benzene	0.175	.006
Naphthalene	0.213	.001
Fluorene	0.267	.005
Anthracene	0.238	.004
Phenanthrene	0.275	.010
2-Methylanthracene	0.336	.006
1-Methylphenanthrene	0.211	.018
Pyrene	0.286	.003
Fluoranthene	0.339	.010
Chrysene	0.336	.010
Triphenylene	0.216	.010
1,2-Benzanthracene	0.354	.002

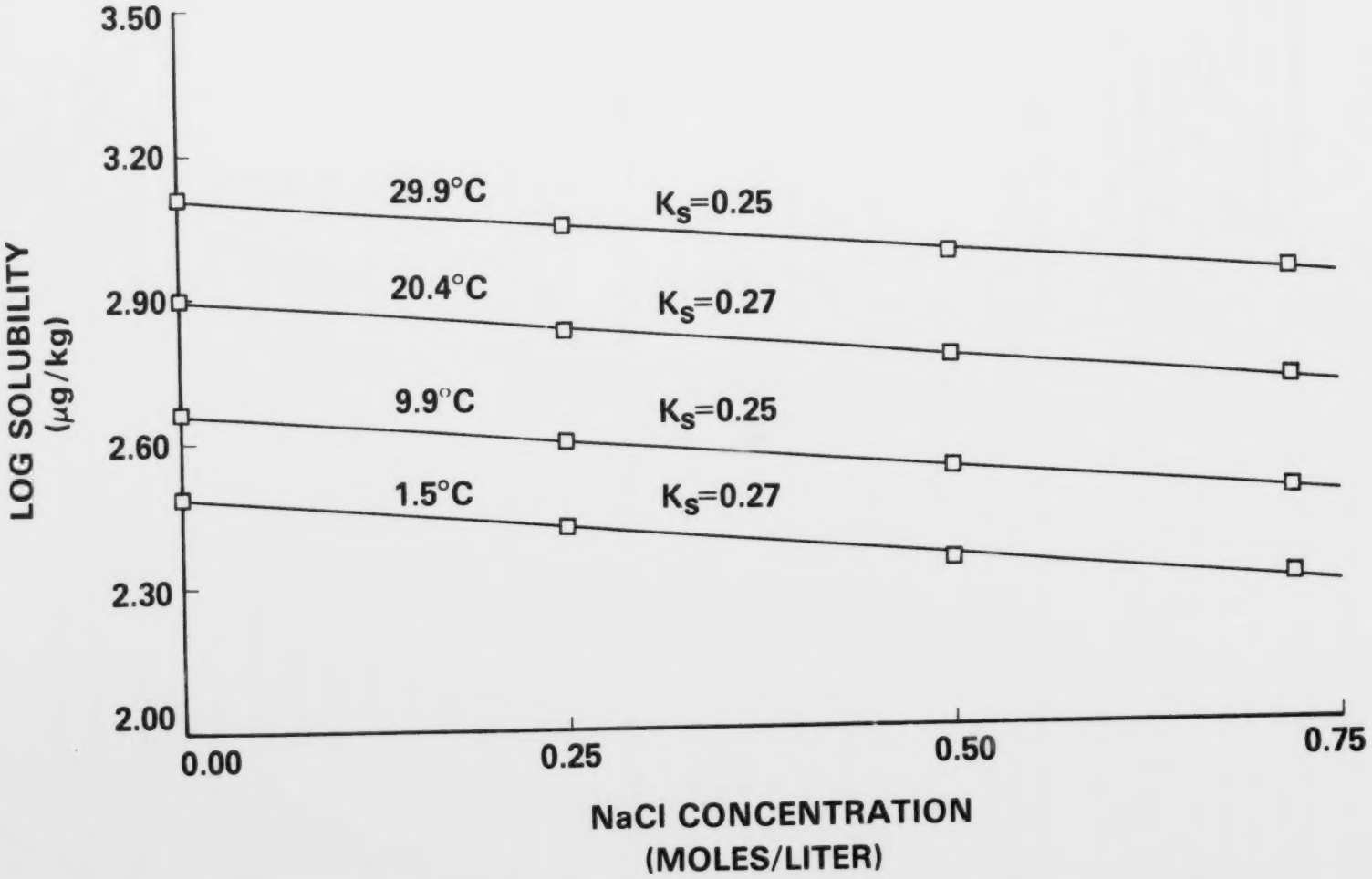


Figure 4. Solubility of phenanthrene as a function of sodium chloride concentration.

The theory developed by McDevitt and Long (35) for the "salting out" of liquid hydrocarbons from aqueous solutions predicts an increase in K_s with increasing liquid molar volume for nonelectrolyte solutes. This relationship seems to also be valid for this series of crystalline compounds with triphenylene again giving anamolous results. (Molar volumes presented in Table 13.)

TABLE 13. CORRELATIONS OF SOLUBILITY WITH MOLECULAR PARAMETERS

	Compound	Carbon No.	Molar Volume[a] (mL)	Molecular Length[b] (A)	-ln(S)
1.	Benzene	6	189	5.5	3.77
2.	Naphthalene	10	125	8.0	8.30
3.	Fluorene	13	153	---	11.5
4.	Phenanthrene	14	159	9.5	12.1
5.	Anthracene	14	160	10.5	15.2
6.	Pyrene	16	172	9.5	14.2
7.	Fluoranthene	16	175	9.4	13.8
8.	1,2 Benzanthracene	18	194	11.8	17.0
9.	Triphenylene	18	190	9.5	17.4
10.	Chrysene	18	194	11.8	18.7

[a]Reported by Davis and Goltbieb in reference 52.

[b]Reported by Klevens in reference 25.

Correlations of Solubility with Molecular Parameters

The aqueous solubility of aromatic hydrocarbons has been shown by Klevens (25) to be related to carbon number, molar volume and molecular length. These parameters along with the molar solubilities (expressed as -lnS) of the compounds studied are presented in Table 13. Figures 5 through 7 demonstrate the relationship between each of these parameters and solubility. These data figures show that there are several compounds whose anamolous behavior makes accurate extrapolations of solubility from these relationships impossible. For example, anthracene and phenanthrene are structural isomers. They, therefore, have identical carbon numbers

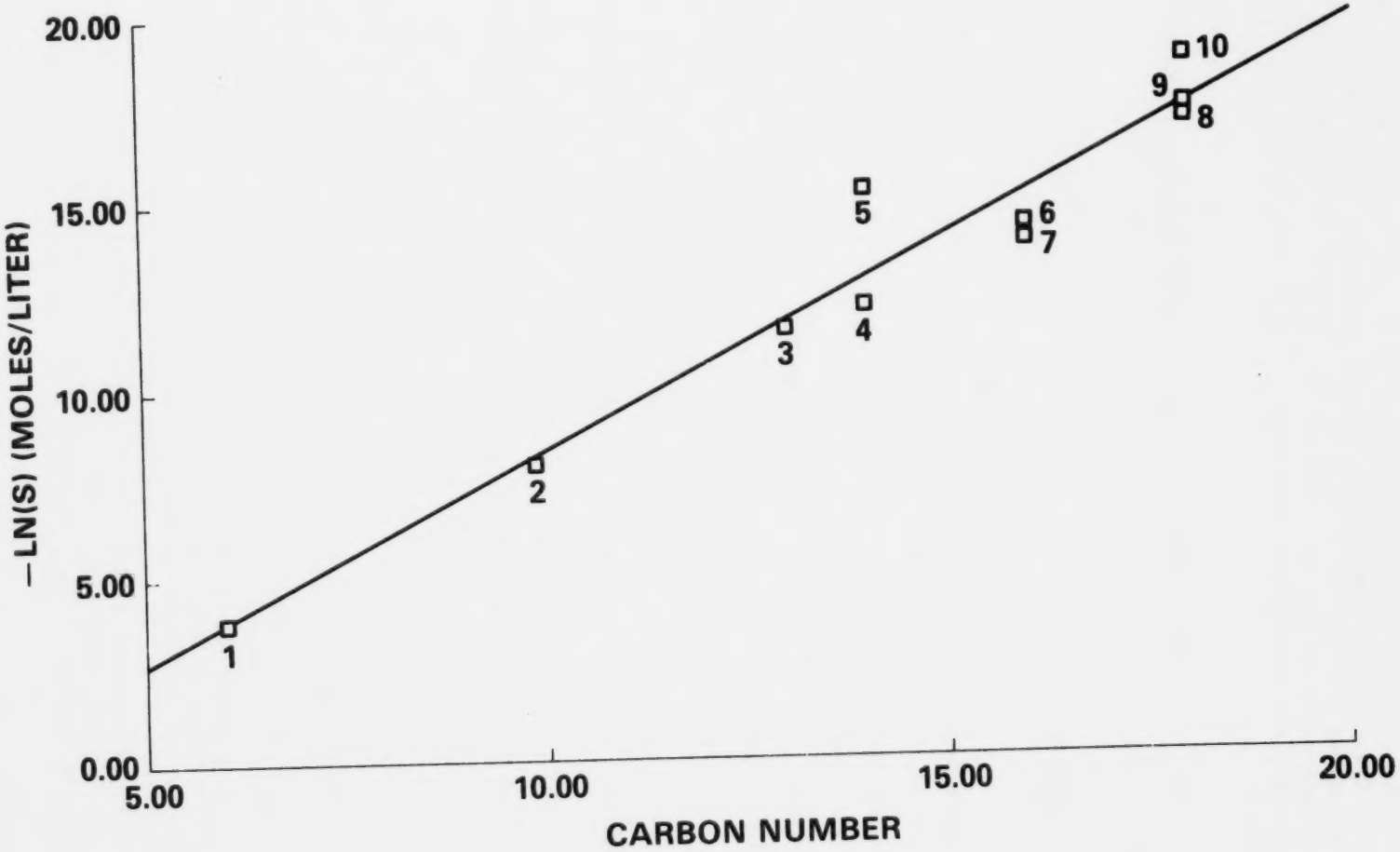


Figure 5. Variation of solubility with carbon number.

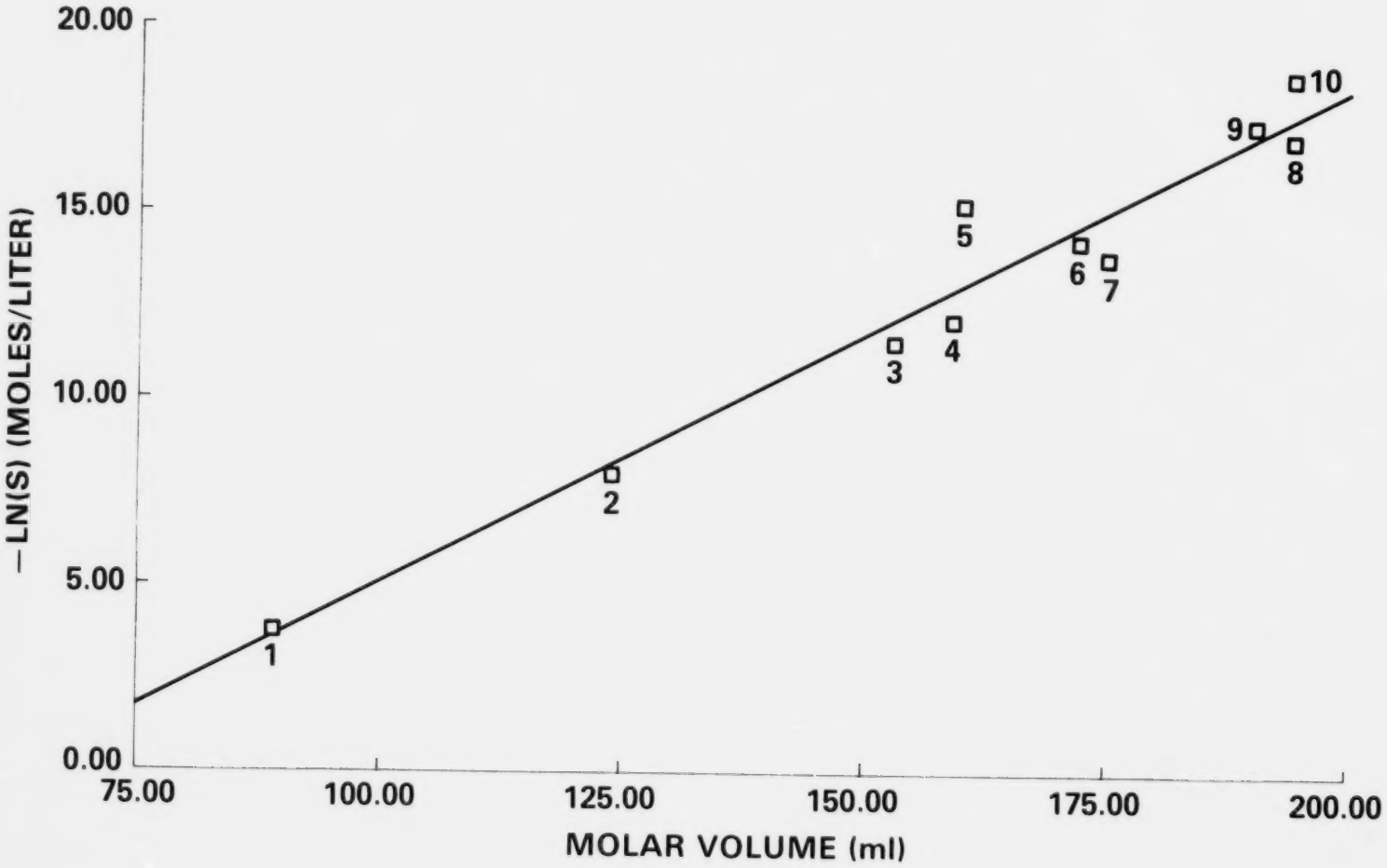


Figure 6. Variation of solubility with molar volume.

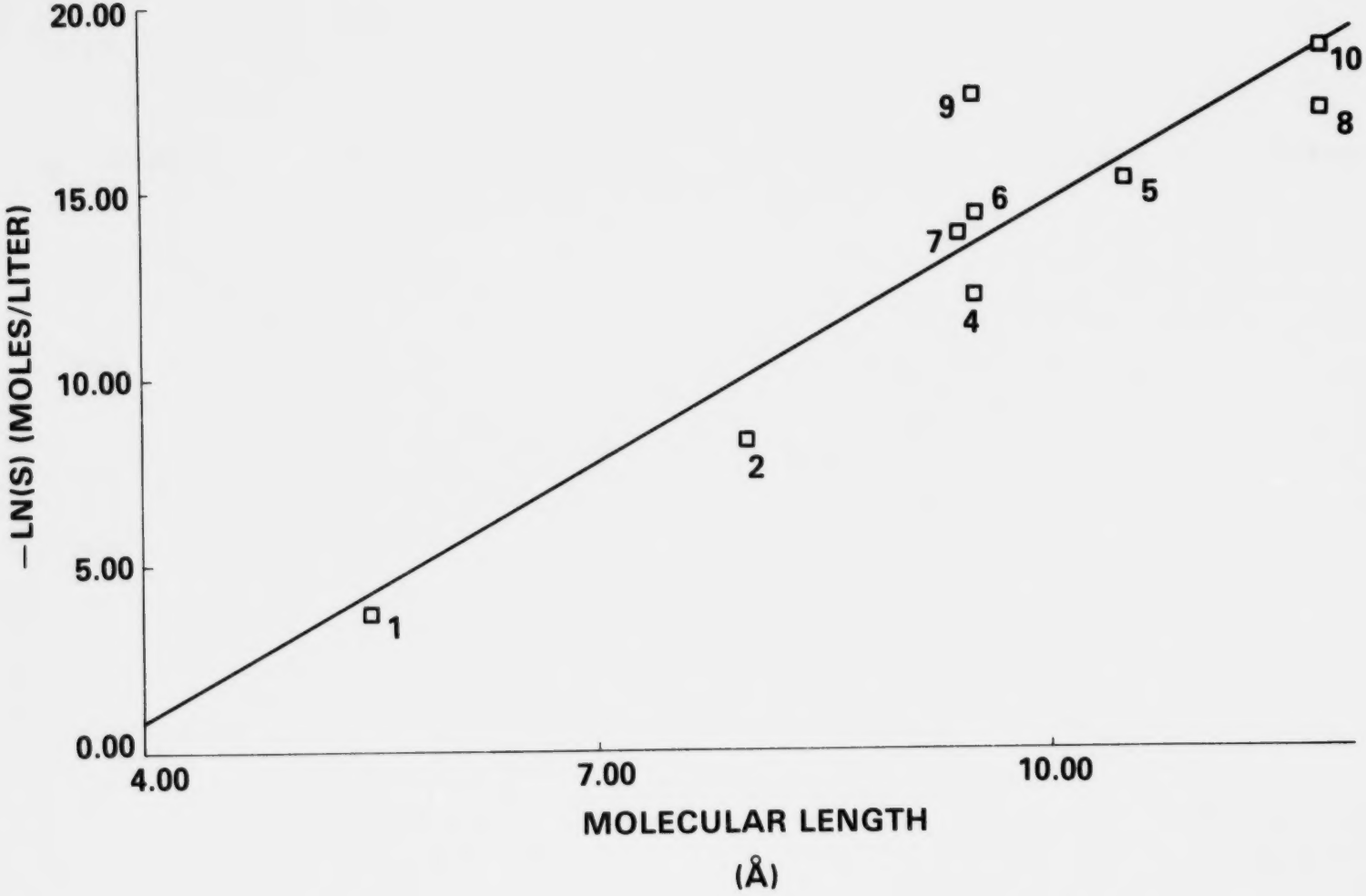


Figure 7. Variation of solubility with molecular length.

and very similar molar volumes. However, their aqueous solubilities differ by more than a factor of twenty. Phenanthrene, fluoranthene, pyrene and triphenylene all have very similar molecular lengths; but their respective aqueous molar solubilities at 25 °C are, 5.6×10^{-6}, 1.0×10^{-6}, 6.8×10^{-7}, 2.8×10^{-8}.

Tsonopoulos and Pransnitz (27) have reported that the hydrocarbon infinite dilution coefficient, γ^{∞}, is the appropriate quantity for correlating the aqueous solubilities of hydrocarbons. They, along with Leinonen et al. (23) and Pierotti et al. (28) have successfully correlated γ^{∞} with carbon number, molar volume, and degree of branching. Recently Mackay and Shiu (26) have correlated the hydrocarbon infinite dilution coefficients of 32 aromatic hydrocarbons (using the super cooled standard state) with carbon number. From this relationship, they derived a parabolic equation from which individual solubilities could be calculated. A comparison of the correlated and experimental solubility values showed that solubilities could be estimated only to within a factor of 3.

Summary

The DCCLC technique is a very rapid, precise and accurate method for determining aqueous solubilities and related parameters for polynuclear aromatic hydrocarbons. The agreement with solubilities and calculated solubility parameters, such as ΔH_s, for which values have been previously reported in the literature help to confirm the validity of this approach. In all cases replicate solubility measurements of the generated PAH solutions at constant temperature were better than ±3 percent and in most cases better than ±1 percent. Quantitative analyses of hexane extracts of the generated solutions by both GC and HPLC have agreed with the DCCLC values to within ±3 percent in all cases.

The lack of an appropriate physical parameter for accurately extrapolating PAH solubilities further enhances the utility of the DCCLC approach. PAH aqueous solubilities can be accurately measured in about the same time that it would take to make an estimation via correlation with a physical parameter.

PAH SORPTION ON SEDIMENTS

Introduction

Recent studies conducted in this laboratory (NBS) and elsewhere have shown that sediments taken from areas that were thought to be pristine and those taken from areas which have been exposed to low levels of petroleum both contain PAH mixtures of similar distribution. The alkyl homologs predominate over the unsubstituted species. Different possible sources of the PAHs in these and other marine sediments have been suggested. These include biosynthesis; petroleum spillage; combustion from mobile and stationary sources, including refuse burning, forest fires, and industrial activity.

There have been suggestions that at least some PAHs originate from biosynthesis of algae (6), plants (41), or various bacteria (42). Hites and Hase (43) have shown, however, that bacteria accumulate but do not biosynthesize PAHs.

The PAHs found on marine sediments may also originate from petroleum. In petroleum, the three and four carbon alkyl homologs predominate. Petroleum derived PAH mixtures are usually very deficient in the unsubstituted parent PAH.

Combustion-produced PAHs transported by air is another likely source of these compounds in marine environment. Low temperature combustion (such as 1100 °K, as in a cigarette) will yield a soot with an abundance of the alkyl substituted PAHs. Blumer and Youngblood (44) have concluded that PAHs found in several recent sediments are likely to have originated from forest fire particulates. Hites (6), however, refutes this conclusion and offers instead the belief that PAH mixtures are initially deposited by anthropogenic sources and then undergo an in situ modification. Hites postulates that the differential water solubility of the higher alkyl homologs versus the unsubstituted species is the mechanism that is responsible for the PAH distributions found on recent sediments. He proposes the following model: After airborne particulate deposition on soil or in water, the lowest homologs continuously fractionate into the water phase to an extent proportional to their solubility (increasing alkylation lowers aqueous solubility), the remaining species, which accumulate on the particulate matter and on sediment, are, therefore, devoid of the lowest homologs, thus increasing the relative abundance of the higher homologs.

Measurement of PAH Sorption by DCCLC

The DCCLC system is also capable of providing a means of characterizing the sorption characteristics of PAHs on solid adsorbents. Since the concentrations of generated PAH solutions are known functions of temperature, PAH sorption data for the adsorbent was determined by placing a column packed with the material to be characterized between the "generator column" and the switching valve. (See Figure 1). A plot of the concentration measured at the exit of the adsorbent column versus time (or volume) provided data pertaining to the kinetics of the sorption process (interpretation of such data are beyond the scope of this work). Equilibrium was defined as that point at which the PAH concentration at the adsorbent column inlet and outlet were the same. At that point the equilibrium uptake was measured by removing the adsorbent from the column and extracting it with diethyl ether. An aliquot of that extract was then analyzed by liquid chromatography.

Results

Table 14 presents some results obtained when using this method for measuring the equilibrium partition coefficient between distilled water and several silica gels. The sorption of phenanthrene is shown to be a function of surface area for these materials. Tables 15 through 18 present the results obtained for the partitioning of a PAH mixture of phenanthrene, 1-methylphenanthrene, anthracene, and 2-methylanthracene on two silica gels

and two Alaskan sediment samples. The absolute values of the partition coefficients (K) vary, but the preferential sorption of the methylated PAHs is evident in all four experiments. These partition coefficients are not simply inverse functions of solubility. The partition coefficient for anthracene is less than that for 1-methylphenanthrene, although 1-methylphenanthrene is more soluble by a factor of 5.

TABLE 14. THE PARTITIONING OF PHENANTHRENE[a] BETWEEN SILICA GEL AND DISTILLED WATER AS A FUNCTION OF NITROGEN SURFACE AREA

N_2 Surface Area[b] (m^2/g)	Concentration Sorbed on Silica (mg/kg)	Partition Coefficient, K ($\frac{\text{conc. sediment}}{\text{conc. water}}$)
2	8 ± 2	8
22	50 ± 4	52
200	95 ± 7	99
400	130 ± 3	135

[a]Phenanthrene aqueous concentration - 0.96 mg/kg.

[b]Surface areas used are those reported by the manufacturer.

All measurements were made at room temperature.

TABLE 15. THE PARTITIONING OF SOME PAHS BETWEEN ZIPAX[a] AND WATER AT ROOM TEMPERATURE

	Concentration in Water (µg/kg)	Concentration on Sediment at Equilibrium (µg/kg)	K ($\frac{\text{Conc. Sediment}}{\text{Conc. Water}}$)
Phenanthrene	710	1790	2.5
1-Methylphenanthrene	114	816	7.2
Anthracene	15.9	25.7	1.6
2-Methylanthracene	8.1	94.0	12

[a]Zipax is a superficially porous adsorbent marketed by the DuPont DeNemours Co., Wilmington, Delaware.

TABLE 16. THE PARTITIONING OF SOME PAHS BETWEEN PORASIL (250)[a] AND WATER AT ROOM TEMPERATURE

	Concentration in Water (µg/kg)	Concentration on Sediment at Equilibrium (µg/kg)	K ($\frac{\text{Conc. Sediment}}{\text{Conc. Water}}$)
Phenanthrene	809	2.93×10^4	36
1-Methylphenanthrene	92.4	1.00×10^3	108
Anthracene	12.0	5.85×10^2	49
2-Methylanthracene	9.18	1.46×10^3	159

[a]Porasil (250) is a totally porous silica material manufactured by Waters Associates, Milford, Massachusetts.

TABLE 17. THE PARTITIONING OF SOME PAHS BETWEEN WATER AND ALASKAN SEDIMENT "A"

	Concentration in Water (µg/kg)	Concentration on Sediment at Equilibrium (µg/kg)	K ($\frac{\text{Conc. Sediment}}{\text{Conc. Water}}$)
Phenanthrene	710	7.3×10^3	10
1-Methylphenanthrene	114	2.3×10^3	20
Anthracene	15.9	3.0×10^2	19
2-Methylanthracene	8.1	2.9×10^2	36

TABLE 18. THE PARTITIONING OF SOME PAHS BETWEEN WATER AND ALASKAN SEDIMENT "B" AT ROOM TEMPERATURE

	Concentration in Water (µg/kg)	Concentration on Sediment at Equilibrium (µg/kg)	K ($\frac{\text{Conc. Sediment}}{\text{Conc. Water}}$)
Phenanthrene	874	3930	4.5
1-Methylphenanthrene	94.8	1185	13
Anthracene	11.7	127	11
2-Methylanthracene	9.80	246	25

These trends in PAH sorption in aqueous systems are not predicted by chromatographic retention on liquid/solid (adsorption) or normal bonded phase-partition chromatographic systems. Table 19 compares the relative chromatographic retention of these four compounds on silica, alumina, and µBondapak NH_2 using hexane as a mobile phase and on µBondapak C_{18} using a water-acetonitrile mobile phase. There is little difference shown in the chromatographic retention of these three condensed ring PAHs on the two classical adsorbents, silica and alumina, or µBondapak NH_2, a new "bonded phase" chromatographic material. However, the trends in the retention of these three condensed ring PAHs on µBondapak C_{18} (a bond phase usually used in the reverse phase mode) closely resembles the trends of the partition coefficients measured for the sorption of these compounds from water onto silica gels and sediments.

TABLE 19. COMPARISON OF (LOG) RETENTION INDICES (I)[a] OF PHENANTHRENE, ANTHRACENE, AND METHYLATED HOMOLOGS ON SEVERAL LIQUID CHROMATOGRAPHIC PACKING MATERIALS

	Silica (45)	Alumina (64)	µBondapak NH_2 (48)	µBondapak (48) C_{18}
Phenanthrene	3.00	3.00	3.00	3.00
1-Methylphenanthrene	3.26	3.18	2.98	3.43
Anthracene	2.97	3.00	2.95	3.02
2-Methylanthracene	--	--	2.92	3.63

[a]The retention indices were calculated as previously described by Popl et al. (45), with the hydrocarbon standards being assigned the following retention indices: benzene 10, naphthalene 100, phenanthrene 1000, benzo(a)anthracene 10,000, and benzo(b)chrysene 100,000. The retention index of an aromatic hydrocarbon was then calculated in a manner analogous to the calculation of Kováts indices for gas chromatography.

Summary

The results of this brief study indicate that there should be much more work directed toward the understanding of the mechanisms of the sorption (partitioning, adsorption, etc.) of slightly soluble components from water onto particulate matter. The DCCLC technique is an excellent tool for conducting such studies.

DEVELOPMENT OF AN AQUEOUS POLYNUCLEAR AROMATIC HYDROCARBON STANDARD REFERENCE MATERIAL

Introduction

The National Bureau of Standards currently issues over 900 Standard Reference Materials (SRMs), with various groups being represented, such as: clinical laboratory standards, trace element standards, nuclear materials, glass viscosity standards, rubber materials, color standards, and coating thickness standards. We are now endeavoring to add to this list an additional group, namely trace organic chemical Standard Reference Materials.

The first SRM from this new group of materials will be an aqueous polynuclear aromatic hydrocarbon (PAH) Standard Reference Material. There are several problems associated with the preparation, storage and handling of aqueous solutions of PAH that previously prevented the development of this SRM. Now, through the use of a dynamic coupled-column liquid chromatographic method developed in this laboratory, we have been able to circumvent these problems. The use of this technique for the preparation and certification of an aqueous PAH SRM will be discussed.

Background

In the fall of 1975, the National Bureau of Standards (NBS) and the Environmental Protection Agency (EPA) jointly sponsored a series of workshops entitled "Standards and Reference Materials for Environmental Analysis Associated with Energy Development". The objective of these workshops was to obtain input to NBS on the methodology and certified standards needed for the accurate analysis of environmental samples associated with the production of alternate fuels.

At the conclusion of these workshops, a number of Standard Reference Materials (SRMs) were recommended by the participants for NBS consideration. One of the SRMs recommended was a polynuclear aromatic hydrocarbon (PAH) in a water matrix. Although many PAH have demonstrated mutagenic properties, this SRM was given a low priority because of the presumed difficulties associated with the preparation and stabilization of such a material.

Problems Associated with the Preparation and Stabilization of a PAH/Water SRM

Preparation of aqueous PAH solutions of known concentration by gravimetric procedures is difficult because of the extremely low aqueous solubilities of PAH. As shown in Table 9 many PAH have aqueous solubilities of less than 500 µg/kg (ppb). Preparation of aqueous solutions of known concentration by

serial dilutions of a more concentrated organic solution is both hazardous and wasteful. After small aliquots are taken, large volumes of organic solvent containing toxic and expensive chemicals remain to be disposed of.

Preservation of stable aqueous solutions of PAH is hampered by adsorptive losses of the PAH to the surfaces of containers and transfer tools. The magnitude of the adsorptive effect is variable and is a function of the manner in which the solutions are handled. The adsorptive properties of three PAH on four different surfaces were shown in Table 5. These results show that losses of PAH from static solutions to surfaces occur in short periods of time. Stirring such solutions only slightly reduces such losses.

Preparation of Standard Aqueous Solutions of Individual PAHs

With the development of the DCCLC technique, accurate preparation of standard aqueous PAH solutions is possible. The aqueous solubility of a compound is a well defined thermodynamic quantity. "Generator columns" loaded with single PAHs produce saturated solutions. The use of generated solutions circumvents the problems that are usually associated with maintaining aqueous PAH solutions, since the solutions need not be generated until they are needed.

Preparation of Aqueous Solutions Containing Several PAH Using "Generator Columns"

Although they do not generate saturated solutions, "generator columns" coated with three or more compounds are of more practical value. The initial attempt to prepare such a column met with only limited success. A column that was composed of fifty milligrams each of phenanthrene, 1-methylphenanthrene, anthracene, and 2-methylanthracene coated on 20 grams of glass beads, was prepared. The results of this experiment are reported in Table 20. After 6 liters of water had been pumped through this "Generator Column" (G-1), equilibrium had not been achieved.

The same four compounds were used in a second attempt to prepare a "generator column" that would be capable of generating a stable solution of these four components. The amounts of each compound comprising the one percent coating on the glass beads was made to be proportional to its aqueous solubility. The results reported in Table 21 demonstrate the feasibility of this approach. After initial conditioning, over six liters of solution was generated with the maximum change being less than 10 percent over that range.

A third "generator column" (G-3), loaded with three compounds was prepared by the same technique used to prepare G-2. The column was purged with 5000 mL of water at 25 °C after which a state of equilibrium was reached. Although the concentrations generated by this column were not equal to the equilibrium saturation concentrations for the individual components, they did not ever change by more than ±5% while more than 6000 ml of water was purged through the column (see Table 22). The concentrations of the individual compounds in the effluent of this column over this interval at 25 °C were:

Anthracene	62.1 ± 1.3 µg/kg
2-Methylanthracene	13.3 ± 0.2
1,2-Benzanthracene	10.8 ± 0.3

TABLE 20. EFFLUENT STABILITY OF "GENERATOR COLUMN" G-1

Water Purge Volume (ml)	Phenanthrene Conc. (µg/kg)	1-Methyl-Phenanthrene Conc. (µg/kg)	Anthracene Conc. (µg/kg)	2-Methyl Anthracene Conc. (µg/kg)
100	610	167	22.1	14.6
500	541	155	26.0	15.9
860	520	148	26.6	15.1
1330	506	150	29.1	15.7
4500	405	157	34.9	15.5
5350	388	162	35.4	15.8
550	380	164	36.1	15.9
6400	377	170	35.2	17.7
$\bar{x}$ (1300-6499 ml)	411 ± 53	161 ± 7.6	34.1 ± 2.9	16.1 ± 8.9
Maximum Range Between High and Low Value	29%	13%	19%	12%

TABLE 21. EFFLUENT STABILITY OF "GENERATOR COLUMN" G-2

Water Purge Volume (ml)	Phenanthrene Conc. (µg/kg)	1-Methyl-Phenanthrene Conc. (µg/kg)	Anthracene Conc. (µg/kg)	2-Methyl Anthracene Conc. (µg/kg)
25	913	96.3	12.1	12.2
550	897	73.6	20.1	9.6
2250	890	71.8	18.4	11.1
3700	906	69.9	16.6	10.2
5200	898	70.8	16.4	10.0
6320	888	74.4	16.0	8.94
7100	903	71.0	17.0	10.3
8100	876	78.1	16.5	9.24
$\bar{x}$ (2250-8100 ml)	894 ± 11	72.7 ± 3.1	16.8 ± 0.9	10.0 ± 0.8
Maximum Range Between High and Low Value	1.8%	8.1%	5.8%	19.5%

TABLE 22. EFFLUENT STABILITY OF "GENERATOR COLUMN" G-3

Water Purge Volume	Anthracene	2-Methyl Anthracene	1,2 Benzanthracene
200	63.6	13.3	15.8
2000	58.9	11.9	14.0
5000	62.0	13.3	10.9
6000	64.1	12.9	11.0
7200	62.8	13.4	10.7
8100	62.2	13.4	11.0
9300	61.7	13.2	10.7
9990	60.6	13.1	10.4
11500	61.0	13.4	11.1
$\bar{x}$ (5000-11,500 mL)	62.1 ± 1.3	13.3 ± 0.2	10.8 ± 0.3
Minimum Range Between High and Low Value	5.5%	3.0%	6.3%

Figure 8 shows that the relationship between ln solubility and temperature is linear for each of the three compounds over the 0-30 °C temperature range. This, indicates that this solution generating process is thermodynamically well behaved and allows one to predict the concentration of each component in the ternary solution, given the temperature.

Preparation of Dilute Organic Standard PAH Solutions

Small volumes of dilute organic solutions may also be accurately prepared by extracting the generated aqueous solutions with the desired volume of an immiscible organic solvent, such as hexane. Since PAH hexane/water distribution coefficients are very large, the concentration of these dilute solutions can be calculated if the volume ratios are known. For example, 5 mL of a 10 (µg/kg) ppb solution of chrysene in hexane could not be prepared gravimetrically. Such a solution would have to be prepared by serial dilutions of a more concentrated solution. This process is both wasteful and hazardous. After an aliquot is taken from the concentrated solution, a large volume of toxic solution will remain to be discarded. However, such a solution can be prepared by extracting 25 mL of a saturated aqueous solution ($\sim$2ppb) of chrysene with 5 ml of hexane. This is only a hypothetical example, but it does demonstrate the utility of using "Generator Columns" to prepare organic PAH solutions of known concentrations indirectly.

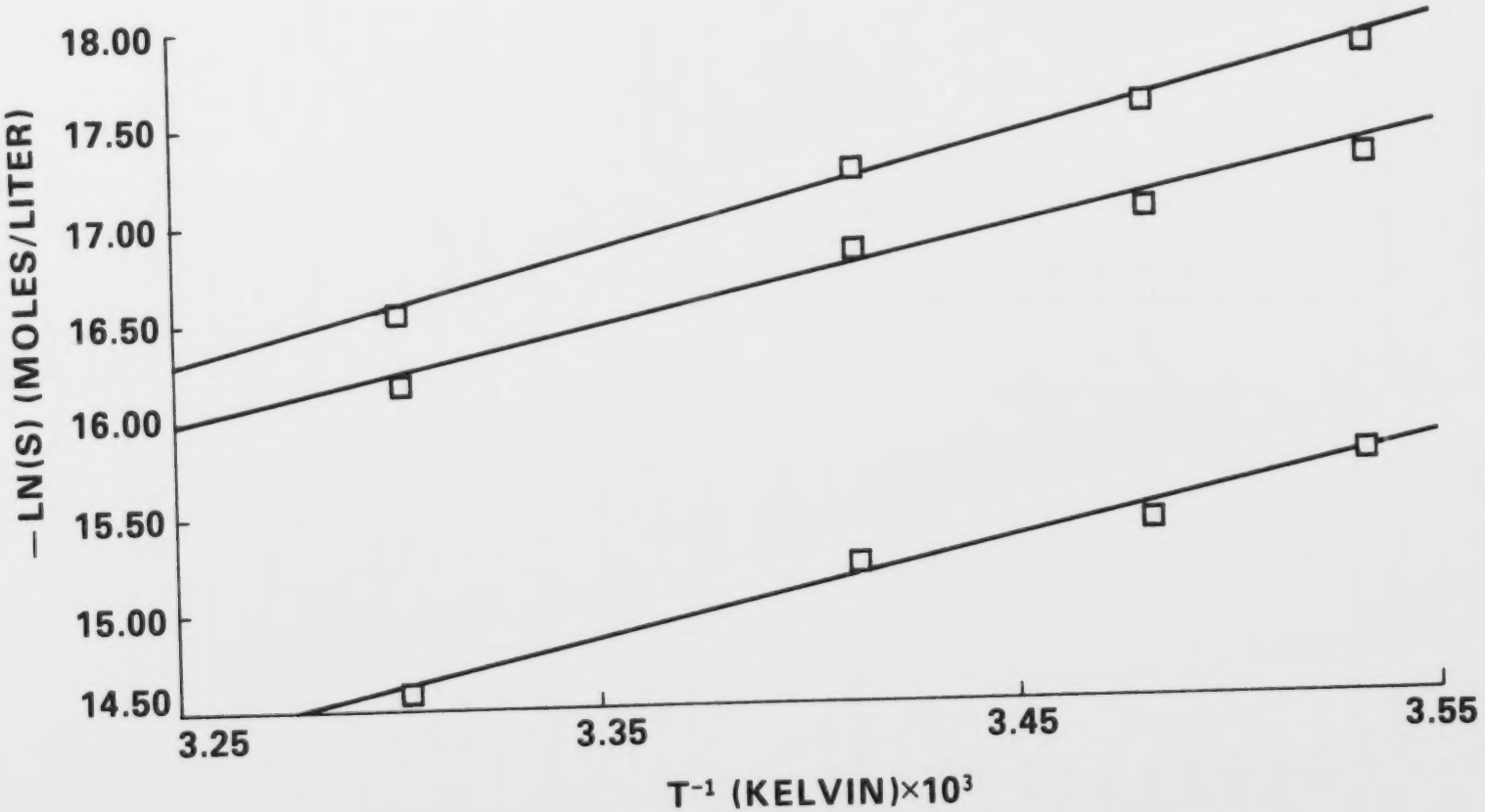


Figure 8. Concentration dependence of components of a ternary solution on temperature.

Evaluation of DCCLC as a Method for the Preparation and Certification of an Aqueous PAH SRM

There are several factors that make the DCCLC approach ideal for the preparation and analysis of very dilute aqueous solutions of individual PAHs. Many of the factors have been discussed earlier in other contexts and will be only referred to here.

1. Saturated solutions are prepared by an equilibrium process. This process has been shown to be reversible and PAH concentrations are independent of the rate of flow through the "generator columns" between 0.1 and 5.0 mL/min.

2. The use of "generator columns" to produce aqueous PAH solutions circumvents the problems that are usually associated with storing such solutions, since the solutions need not be generated until they are needed.

3. The concentration of the generated aqueous solutions are a function of temperature, and may be expressed in terms of least squares fits of the concentration as a function of temperature to within ±2% of the experimentally determined values between 5 and 30 °C (see Appendix B).

4. Both the short and long term precision with which aqueous PAH solutions can be generated appear to be $\leq$2% (see Table 8).

5. Shelf storage of "generator columns" does not seem to present a problem. They have been shown to be stable for longer than one and a half years and through more than 100 liters of aqueous purge.

6. DCCLC is a rapid and accurate method for analyzing the generated dilute aqueous PAH solutions. Analytical errors due to adsorption are minimized in DCCLC because the solution is extracted and concentrated, on line, in less than 500 ms after generation. It has been estimated that this analytical method has an uncertainty of less than two percent.

REFERENCES

1. Tsonopoulos, C., and J. Prausnitz, Ind. Eng. Chem. Fundam., 10:503, 1971.

2. LeFeuvre, A. Water and Water Pollution Handbook. Vol. 1, L. L. Ciaccio, Ed. Marcel Dekker, Inc., New York, 1971. p. 263.

3. Peak, E., and G. Hodgson. J. Amer. Oil Chemists Soc., 215, 1966.

4. Ben-Naim, A. J. Chem. Phys., 57:5257, 1972.

5. Ben-Naim, A. Water and Aqueous Solutions. R. A. Horne, Ed., (Wiley, New York, 1972. p. 425.

6. Hites, R. Proceedings of the "Source, Effects and Sinks of Hydrocarbons in the Aquatic Environment" Symposium, American University, Washington, DC, Aug. 1976.

7. MacKay, D., and W. Shiu. Can. J. Chem. Eng., 53:239, 1975.

8. AcAuliffe, C. J. Phys. Chem., 70:1274, 1966.

9. Sutton and Clader. J. Chem. Eng. Data, 20:320, 1975.

10. Arnold, D., C. Plank, and E. Erickson. Chem. Eng. Data Serv., 3:253, 1958.

11. Bohon, R., and W. Claussen. J. Amer. Chem. Soc., 73:1571, 1951.

12. Vermillion, H. Ph.D. Thesis, Duke University, Durham, NC, 1939.

13. Stearns, R., H. Oppenheimer, E. Simon, and W. Harkins. J. Chem. Phys., 14:496, 1947.

14. Hill, A. J. Amer. Chem. Soc., 44:1163, 1922.

15. Franks, F., M. Gent, and H. Johnson. J. Chem. Soc., 2716, 1973.

16. Hayashi, M., and T. Sasaki. T. Bull. Chem. Soc. Japan, 29:857, 1956.

17. Booth, H., and H. Everson. Ind. Eng. Che, 40:1491, 1948.

18. Morrison, T., and F. Billet. J. Chem. Soc, 3819, 1952.

19. Horiba, S. Mem. Coll. Eng. Kyoto Imp. Univ. 1, 49, 1914.

20. Fühner, H. Che. Ber..., 57:510, 1924.

21. Andrews, L., and R. Keefer. J. Am. Chem. Soc., 72:5034, 1950.

22. MacKay, D., W. Shiu, and A. Wolkoff. Gas Chromatographic Determination of Low Concentrations of Hydrocarbons in Water, in Water Quality Parameters. ASTM STP 573, Philadelphia, Pennsylvania, 1975.

23. Leinonen, P., D. MacKay, and C. Philips. Can. J. Chem. Eng., 49:288, 1971.

24. Davis, W., M. Krohl, and G. Clower. J. Am. Chem. Soc., 64:108, 1942.

25. Klevens, H. J. Phys. Colloid Chem., 54:283, 1950.

26. MacKay, D., and W. Shiu. Accepted for Publication in J. Chem. Eng. Data.

27. Tosonopoulos, C., and J. Prausnitz. Ind. Eng. Chem. Fundam., 10:593, 1971.

28. Pierotti, G., C. Deal, and E. Derr. Ind. Eng. Chem., 51:95, 1959.

29. Wauchope, R., and F. Getzen. J. Chem. Eng. Data, 17:38, 1972.

30. Weimer, R., and J. Prausnitz. J. Chem. Phys., 42:3643, 1965.

31. Schwarz, F. J. Chem. Eng. Data, 22:273, 1977.

32. Eisenbrand, J., and K. Baumann. Z. Lebensm. Unters. Forsch., 144:312, 1970.

33. McAuliffe, C. Chem. Tech., 1:46, 1971.

34. Brown, R., and S. Waskik. J. Res. NBS (US), 78A, 453, 1974.

35. McDevit, W., and F. Long. J. Amer. Chem. Soc., 74:1773, 1952.

36. Locke, D. J. Chromatog. Sci., 12:433, 1974.

37. Peake, E., and G. Hodgson. J. Amer. Oil Chemists Soc., 44:696, 1967.

38. May, W., S. Chesler, S. Cram, B. Gump, H. Hertz, D. Enagonio, and S. Dyszel. J. Chromatogr. Sci., 13:535, 1975.

39. May, W., Ph.D. Dissertation, University of Maryland, College Park, MD, 1977, pp. 34-40.

40. Setschenow, J. Z. Physik Chem., 4:117, 1889.

41. Hancock, J., H. Applegate, and J. Dodd. Atoms. Environ., 4:363, 1970.

42. Niaussat, P., C. Auger, and L. Mallet. C. R. Acad. Sci. (PARis), 270D:1042, 1970.

43. Hase, A., and R. Hites. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science Pub., Ann Arbor, Michigan, 1976.

44. Blumer, M., and W. Youngblood. Science, 188:53, 1975.

45. Popl, M., V. Dolansky, and J. Mostecky. J. Chromatogr., 117:117, 1976.

46. Popl, M., V. Dolansky, and J. Mostecky. J. Chromatogr., 91:649, 1974.

47. Popl, M., V. Dolansky, and J. Coupek. J. Chromatogr., 130:195, 1977.

48. Wise, S., S. Chesler, H. Hertz, L. Hilpert, and W. May. Anal. Chem. 49, 2306, 1977.

49. Instruction Manual #4930 for CAHN Electrobalance Model "4700".

50. NBS Circular C434 (1941), US Government Printing Office.

51. The International System of Units (SI), NBS Special Publication 330.

52. Davis, H., and S. Gottlieb. Fuel, 8:37, 1962.

APPENDIX A

PROCESSES THAT AFFECT THE ACCURACY OF DYNAMIC COUPLED COLUMN LIQUID CHROMATOGRAPHY

This section presents a brief discussion of the major processes that affect the accuracy of the DCCLC technique. They are:

A-1 "Extractor Column" Extraction Efficiency;

A-2 Measurement of Sample Volume;

A-3 Calibration of Sample Loop;

A-4 Preparation of Standard Solutions.

This chapter also includes:

A-5 Calculation of Detector Response Factors;

A-6 Calculation of Concentration.

A-1 "Extractor Column" Extraction Efficiency

Extraction of the PAHs from the generated solutions was accomplished by pumping volumes varying between 5.0 and 25.0 mL through the "extractor column." Over this range, extraction efficiencies are quantitative for eleven of the twelve compounds studied in this investigation. Benzene was not extracted efficiently by the extractor column. The solubility of benzene was, therefore, determined by direct injection of 23.2 µL of the generated solutions via a sample loop.

The extraction efficiencies for 5, 10, and 25 mL volumes of benzene, naphthalene, fluorene, and phenanthrene are given below.

Compound	Extraction Efficiency (%) 5 mL	10 mL	25 mL
Benzene	60.0 ± 5.0	4.3 ± 0.9	3.1 ± 1.2
Naphthalene	101.4 ± 2.2	98.8 ± 1.0	98.5 ± 0.5
Fluorene	99.5 ± 1.0	98.4 ± 1.1	98.6 ± 1.2
Phenanthrene	99.5 ± 0.6	98.1 ± 1.5	98.7 ± 0.9

It has been shown elsewhere (39) that retention on, and hence the extraction efficiency of C_{18} packed columns is a function of carbon number. Extraction of the eight larger PAHs studied in this investigation are, therefore, also quantitative.

A-2 Measurement of Sample Volume[1] (See Figure 1)

The volume of saturated solution extracted was determined by and placing the sample valve in the "Extract" position collecting a designated volume of the effluent from the "Extractor Column" in a class "A" 5, 10, or 25 mL volumetric flask. After the volumetric flask had been filled, the sample valve was manually switched to the Analyze position, thus diverting the saturated solution to waste.

The uncertainty associated with this process was dependent on human reflexes. One stroke of the generator pump (Milton Roy Controlled Volume mini-Pump) is .05 mL. If we assume that the volumetric flasks could be reproducibly filled to within one stroke of the generator pump, then the maximum uncertainty associated with the measurement of sample volume is ± 1.0 percent (.05/5.0 mL). This is a very liberal estimate and is equivalent to a very slow reaction time of 0.6 seconds at the maximum flow rate used, 5 mL/min.

A-3 Calibration of the Sample Loop

The volume of the sample loop was determined by an indirect gravimetric procedure. The loop was initially filled with mercury. The mercury was swept from the loop into a tarred weighing dish with approximately 1 mL of pentane. Since mercury and pentane are not miscible, the bulk of the pentane was decanted and the remainder was allowed to evaporate. This process was repeated four times, yielding the following results:

Mass of Mercury displaced from loop

0.3097 grams
0.3167 grams
0.3128 grams
0.3178 grams

$\bar{x}$ 0.3143 ± 1.2 percent grams.

The density of mercury at room temperature is 13.538 g/mL. The volume of the loop was then determined to be 23.2 ± 0.3 µL. Since determination by mass is a definitive method, the errors associated with this determination are random and associated with the ability to reproducibly fill the loop. The accuracy is then the precision with which the mass measurements can be made and is equal to 1.2 percent.

A-4 Preparation of Standard Solutions

Standard solutions of the aromatic hydrocarbons studied in this investigation were prepared by the Direct method. Solutes were weighed on a Cahn

[1] The density of water varies from 0.9960 g/mL at 30° to 1.0000 g/mL at 5 °C. This represents a maximum change in mass/volume of 0.4 percent. In this investigation, it is assumed that one liter of water has a mass of one kilogram.

Electrobalance, dissolved in acetonitrile and made up to a 500 ml volume in a class "A" volumetric flask.

The uncertainty involved in weighing the solutes was small. The balance has a certified accuracy of 5×10^{-4} or 0.05 percent (49). Class "A" 500 mL volumetric flasks have tolerances of less than 0.05 percent (50). The uncertainty associated with the preparation of these solutions is estimated to be less than 0.1 percent.

A-5 Calculation of Response Factors

Detector response factors for the 12 compounds studied in this investigation were determined by injecting 23.2 µL of standard solutions of the compounds into the liquid chromatographic system. These response factors are presented below.

Compound	Response Factor[a] ($\frac{\text{area units}}{\text{ng}}$)
Benzene	20.14 ± 0.22
Naphthalene	184.0 ± 1.18
Fluorene	1071 ± 10
Anthracene	7123 ± 66
Phenanthrene	2890 ± 14
2-Methylanthracene	10647 ± 95
1-Methylphenanthrene	3042 ± 32
Fluoranthene	659.7 ± 8
Pyrene	463.0 ± 3
1,2-Benzanthracene	1479 ± 10
Crysene	2063 ± 15
Triphenylene	3081 ± 10

[a]Calculated from areas obtained when using Perkin Elmer "System I" electronic integrator with a chromatographic flow rate of 2.77 mL/min.

$$\text{Response Factor} = \frac{\text{Area}}{(23.2\ \mu\text{L})\ (\text{Conc. Std.})\ (\text{Purity of PAH})}$$

A-6 Calculation of Concentration

The concentration of the aromatic hydrocarbons in the aqueous solutions was calculated from the following equation:

$$\text{Concentration } (\mu g/kg \text{ or ppb}) = \frac{\text{Area}}{(\text{R.F.})(\text{Sample Volume})}$$

Area - Area under the chromatographic peak as determinded by the electronic integrator.

R.F. - Response Factor (area/ng)

Sample Volume - Size of aqueous sample analyzed in mL (grams).

APPENDIX B

VARIATION OF SOLUBILITY WITH TEMPERATURE

The equations relating aqueous solubility to the temperature that were presented in Section 3 were derived from the data presented in this section. Experimental values of the solubilities between 5 and 30 °C are given in Tables B-1 through B-12 along with the standard deviations associated with each measurement. Each table is accompanied by a plot of a least squares fit of the solubility to temperature.

The SI unit for concentration is moles per cubic meter (mol/m^3). Mole (mol) is the base SI unit for the amount of substance. Cubic Meter (m^3) is a derived unit for volume. The use of a regularly formed multiples such as cubic centimeter and cubic decimeter are also allowed. The special name, liter (51) has been approved for use instead of cubic decimeter, but it's use is restricted to the measurement of liquids and gases.

The PAH solubilities reported in the tables are expressed in both the SI unit mol/liter and metric units mg/kg or µg/kg. The concentration axes for the least squares fits of the solubility to temperature are labeled as either parts per million (ppm) or parts per billion (ppb). Since the density of water between 4 and 30° is essentially constant and equal to 1.000, one liter of water has a mass of one kilogram (kg). Thus µg/kg equals ppb and mg/kg equals ppm.

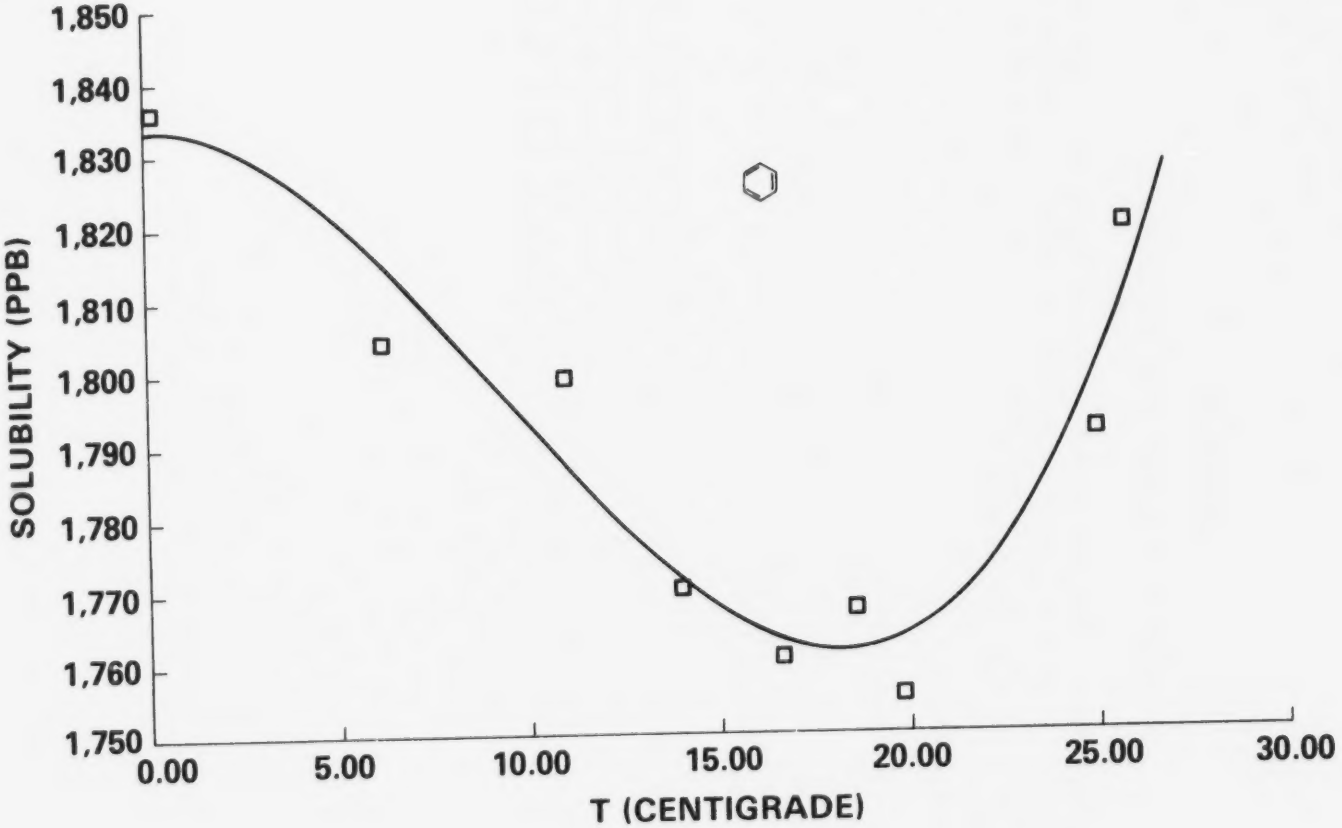


FIGURE B-1. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF BENZENE.

TABLE B-1. BENZENE

Solubility = $0.0247t^3 - 0.6838t^2 + 0.3166t + 1833$ (mg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-2})	Concentration Measured (mg/kg)	Concentration* Calculated (mg/kg)
0.2	2.35	1836 ± 12	1833
6.2	2.31	1804 ± 2	1815
11.0	2.30	1799 ± 13	1787
14.0	2.27	1770 ± 13	1771
16.9	2.26	1762 ± 10	1762
18.6	2.26	1767 ± 5	1761
25.0	2.29	1791 ± 10	1799
25.8	2.33	1819 ± 21	1810

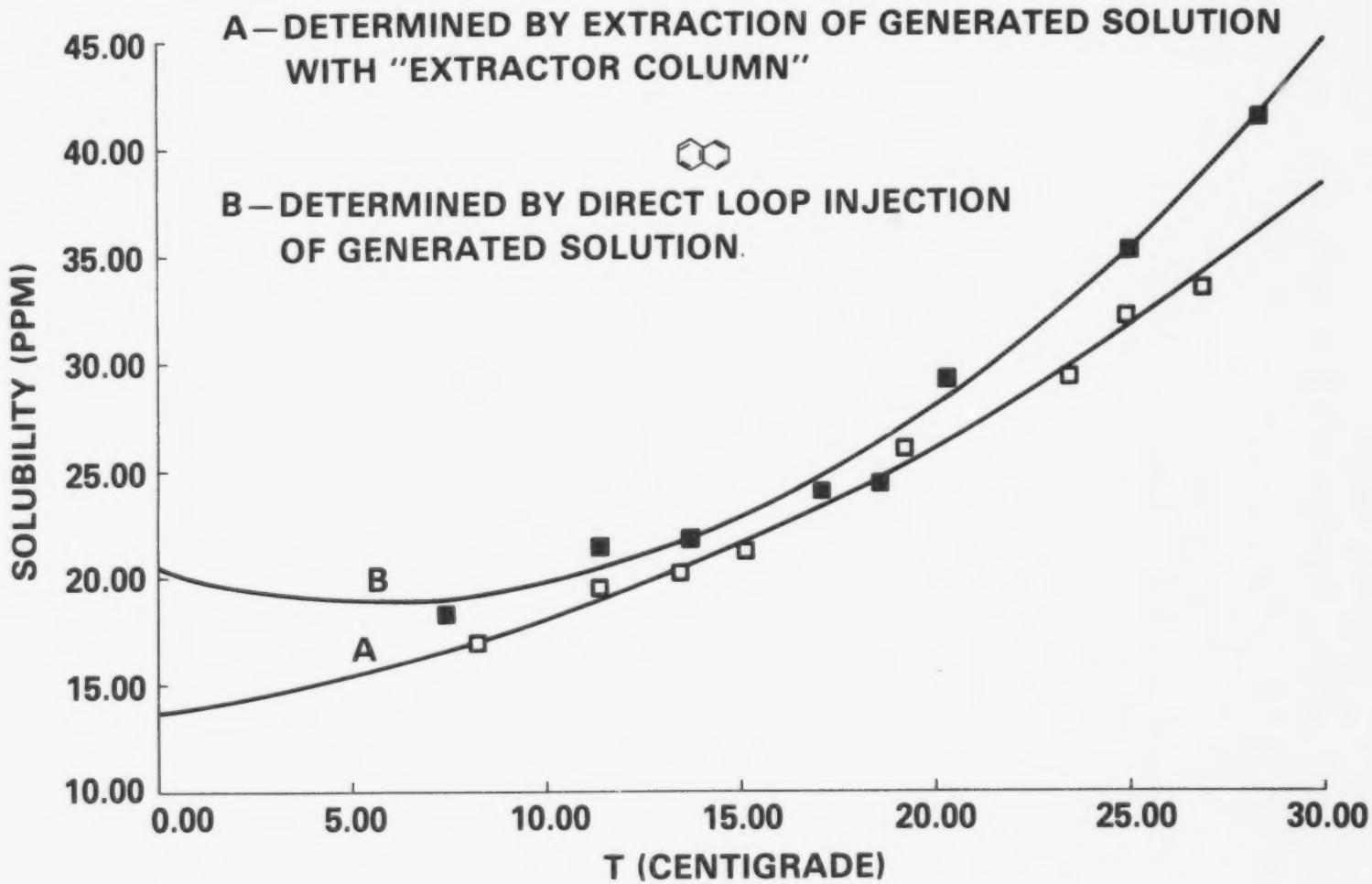


FIGURE B-2. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF NAPHTHALENE.

TABLE B-2. NAPHTHALENE

Solubility = $0.0189t^2 + 0.2499t + 13.66$ (mg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-4})	(mg/kg)	Concentration* Calculated (mg/kg)
27.0	2.66	34.15 ± 0.47	34.16 *
25.0	2.49	31.91 ± 0.30	31.69
23.4	2.30	29.47 ± 0.21	29.83
19.3	2.01	25.79 ± 0.31	25.51
15.1	1.68	21.48 ± 0.11	21.73
13.4	1.59	20.37 ± 0.05	20.39
11.5	1.50	19.23 ± 0.20	19.02
8.2	1.32	16.91 ± 0.26	16.97

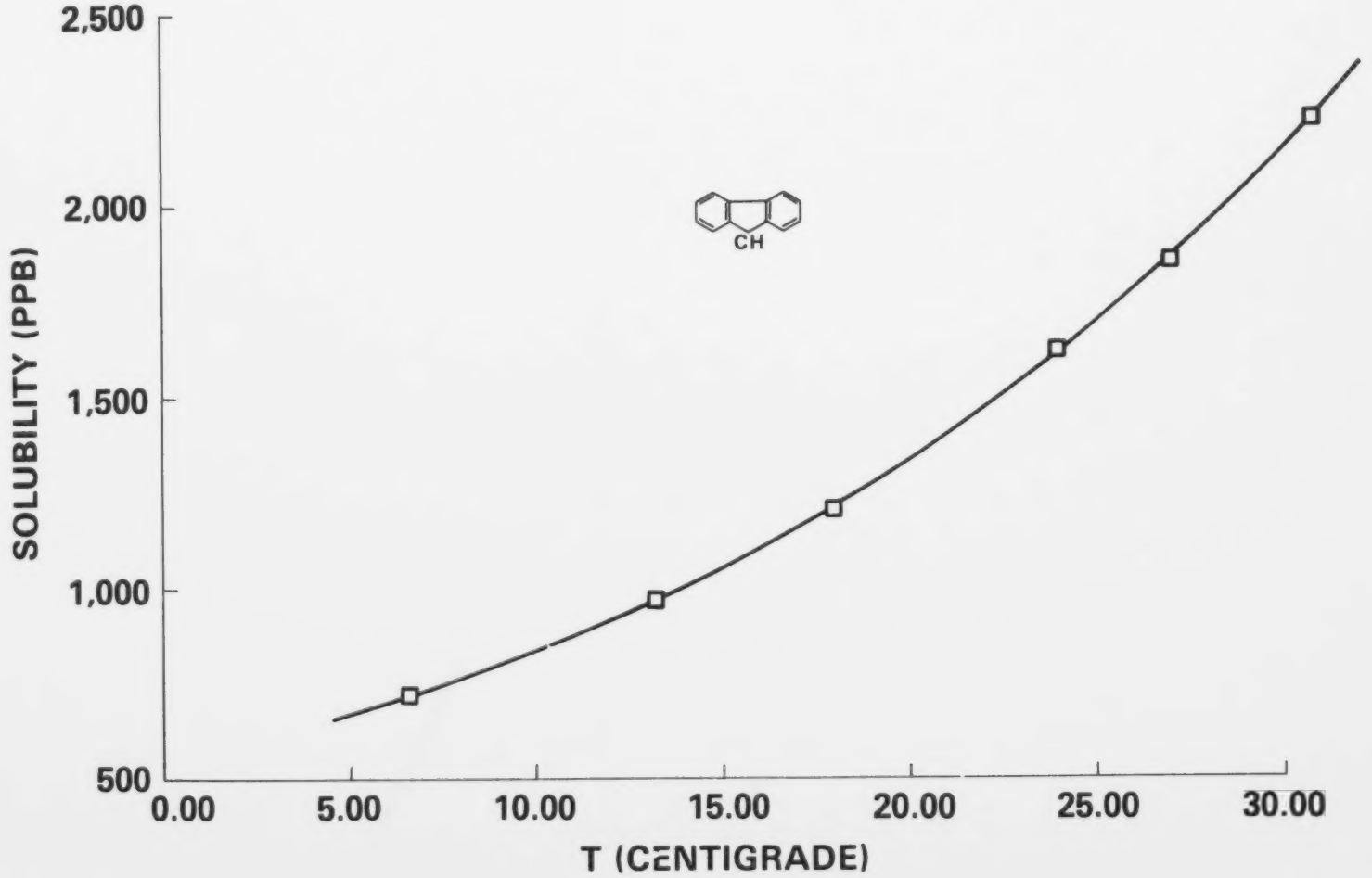


FIGURE B-3. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF FLUORENE.

TABLE B-3. FLUORENE

Solubility = $0.0185t^3 + 0.4543t^2 + 22.76t + 543.3$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-6})	(µg/kg)	Concentration* Calculated (µg/kg)
31.1	13.5	2248 ± 5.0	2246
27.0	11.1	1845 ± 4.9	1853
24.0	9.72	1616 ± 6.0	1607
18.0	7.24	1203 ± 1.1	1208
13.2	5.82	967.3 ± 9.7	965.4
6.6	4.32	718.4 ± 0.7	178.6

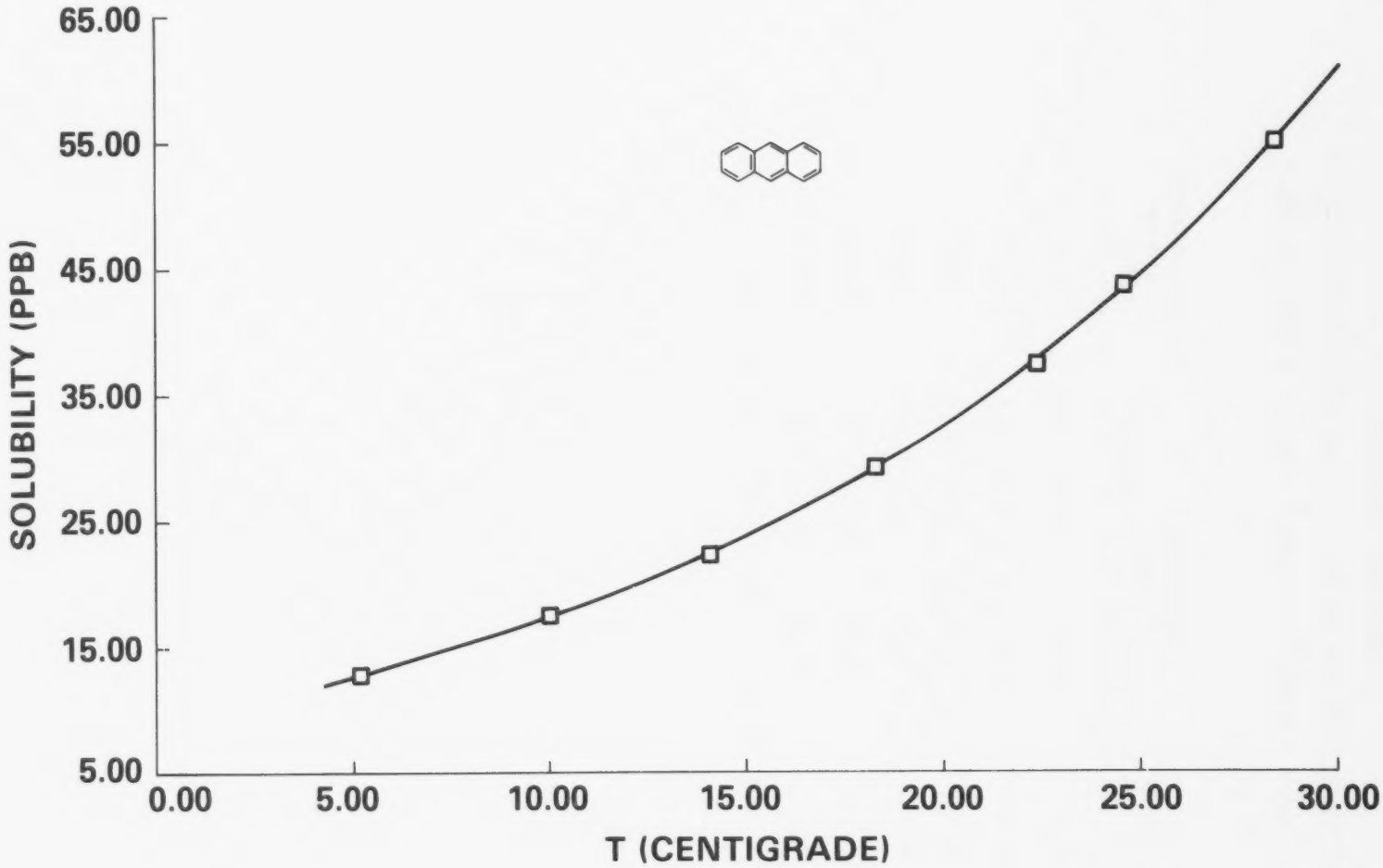


FIGURE B-4. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF ANTHRACENE.

TABLE B-4. ANTHRACENE

Solubility = $0.0013t^3 - 0.0097t^2 + 0.8886t + 8.21$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-7})	(µg/kg)	Concentration* Calculated (µg/kg)
28.7	3.13	55.7 ± 0.7	55.8
24.6	2.44	43.4 ± 0.1	43.1
22.4	2.09	37.2 ± 1.1	37.5
18.3	1.63	29.1 ± 0.6	29.0
14.1	1.25	22.2 ± 0.1	22.3
10.0	0.98	17.5 ± 0.3	17.4
5.2	0.71	12.7 ± 0.4	12.7

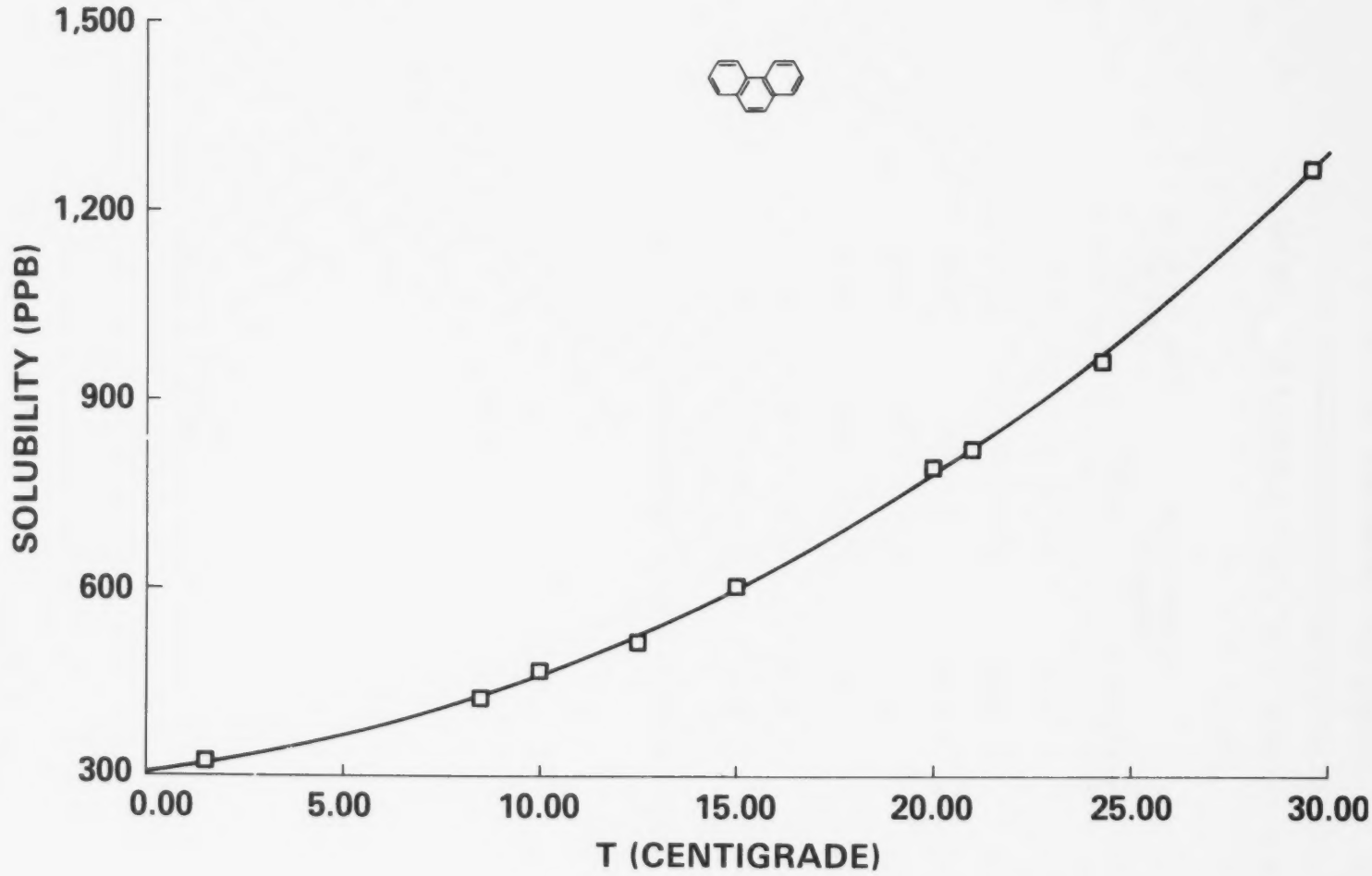


FIGURE B-5. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF PHENANTHRENE.

TABLE B-5. PHENANTHRENE

Solubility = $0.0025t^3 + 0.8059t^2 + 5.413t + 324$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-6})	Concentration Measured (µg/kg)	Concentration* Calculation (µg/kg)
29.9	7.16	1227 ± 11	1274
24.3	5.36	955 ± 1	967
21.0	4.58	816 ± 8	816
20.0	4.42	787 ± 2	775
15.0	3.37	601 ± 7	595
12.5	2.87	512 ± 1	523
10.0	2.63	468 ± 2	461
8.5	2.37	423 ± 4	430
4.0	1.97	361 ± 1	359

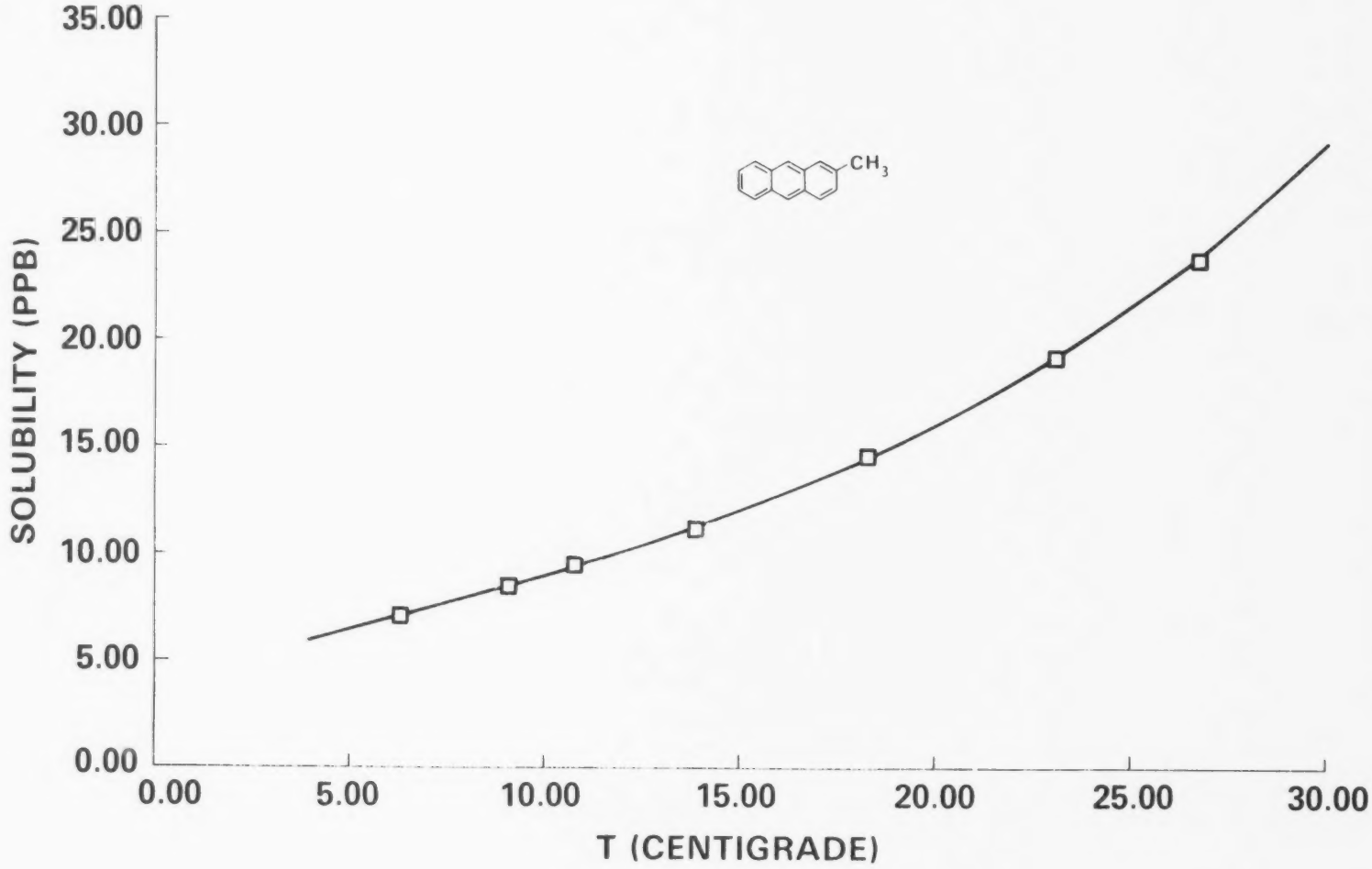


FIGURE B-6. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF 2-METHYLANTHRACENE.

TABLE B-6. 2-METHYLANTHRACENE

Solubility = $0.0011t^3 - 0.0306t^2 + 0.8180t + 2.79$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-7})	(µg/kg)	Concentration* Calculation (µg/kg)
31.1	1.67	32.1 ± 0.3	32.0
27.0	1.26	24.2 ± 0.1	24.4
23.1	0.994	19.1 ± 0.6	19.0
18.3	0.754	14.5 ± 0.1	14.3
13.9	0.575	11.1 ± 0.3	11.2
10.8	0.490	9.43 ± 0.37	9.45
9.1	0.441	8.48 ± 0.09	8.52
6.3	0.367	7.06 ± 0.18	7.00

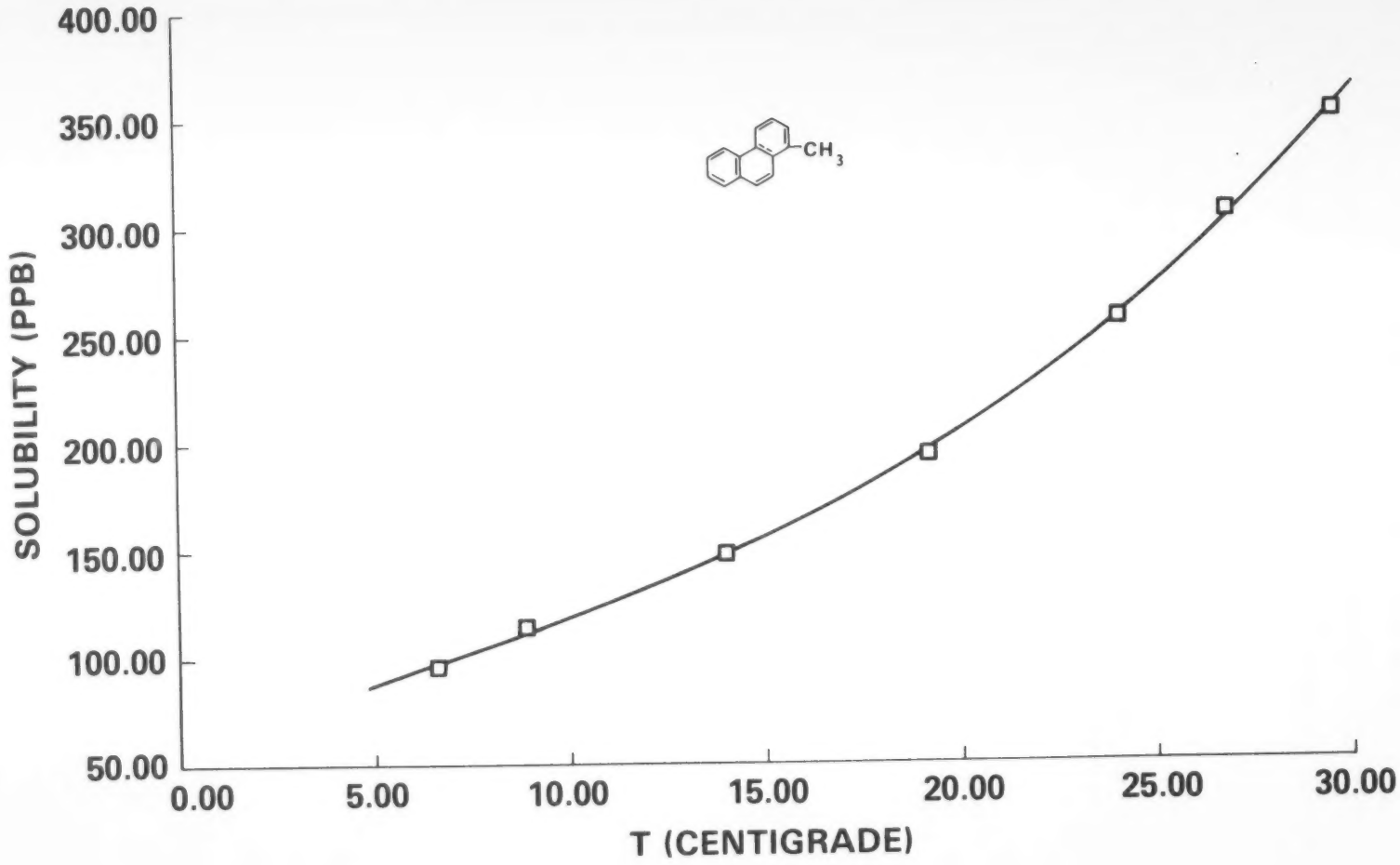


FIGURE B-7. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF 1-METHYLPHENANTHRENE.

TABLE B-7. 1-METHYLPHENANTHRENE

Solubility = $0.0074t^3 - 0.0858t^2 + 5.785t + 62.9$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-6})	(µg/kg)	Concentration* Calculated (µg/kg)
29.9	1.85	355 ± 2	357
26.9	1.58	304 ± 1	302
24.1	1.32	255 ± 5	257
19.2	1.01	193 ± 1	195
14.0	0.765	147 ± 1	147
8.9	0.594	114 ± 4	111
6.6	0.495	95.2 ± 0.2	97.3

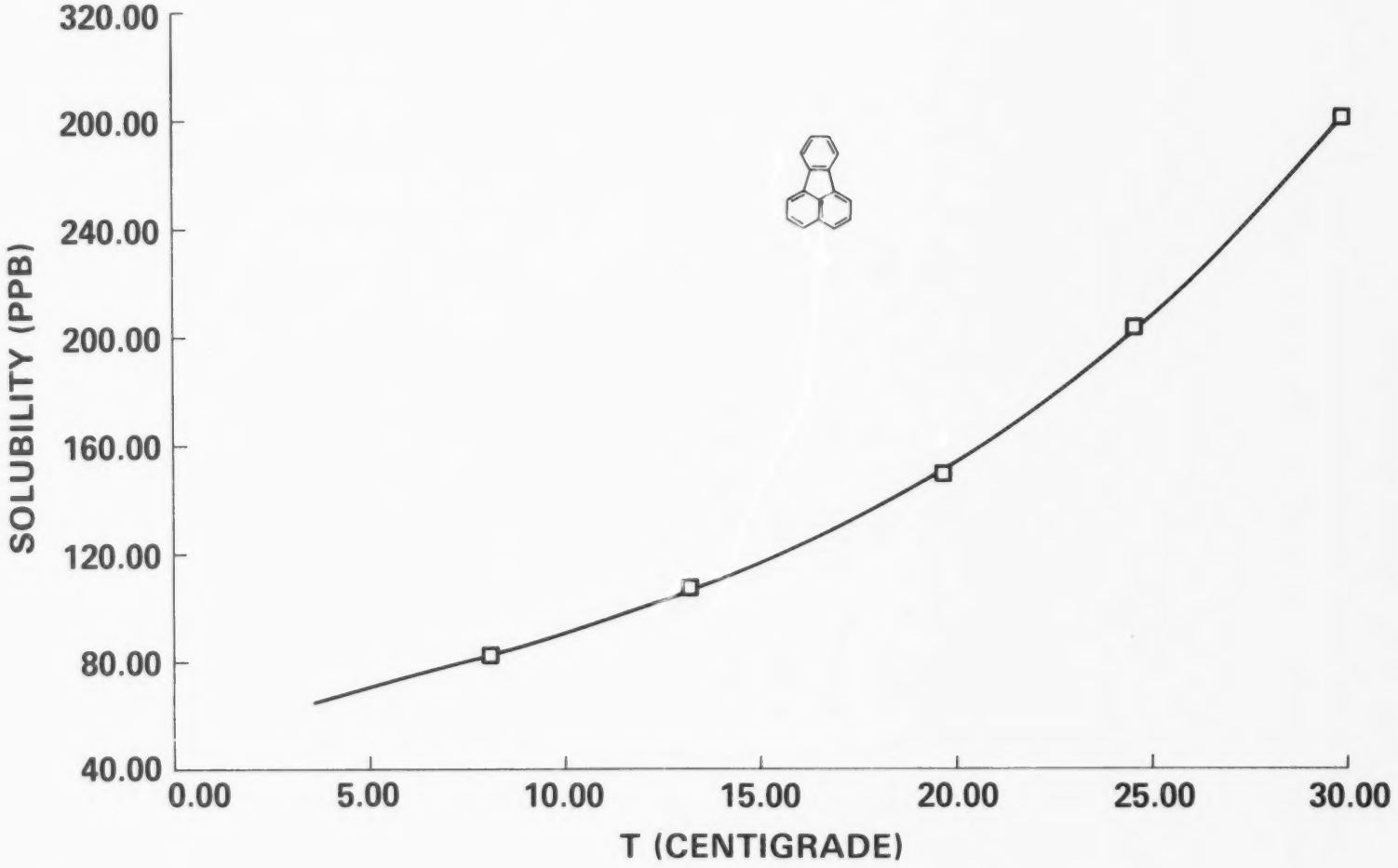


FIGURE B-8. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF FLUORANTHENE.

TABLE B-8. FLUORANTHENE

Solubility = $0.0072t^3 - 0.1047t^2 + 4.322t + 50.4$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-7})	(µg/kg)	Concentration* Calculation (µg/kg)
29.9	13.8	279.3 ± 5.9	280
24.6	10.0	202.7 ± 0.2	201
19.7	7.33	148.3 ± 0.1	150
13.2	5.29	107.0 ± 0.4	106
8.1	4.05	82.0 ± 2.1	82.3

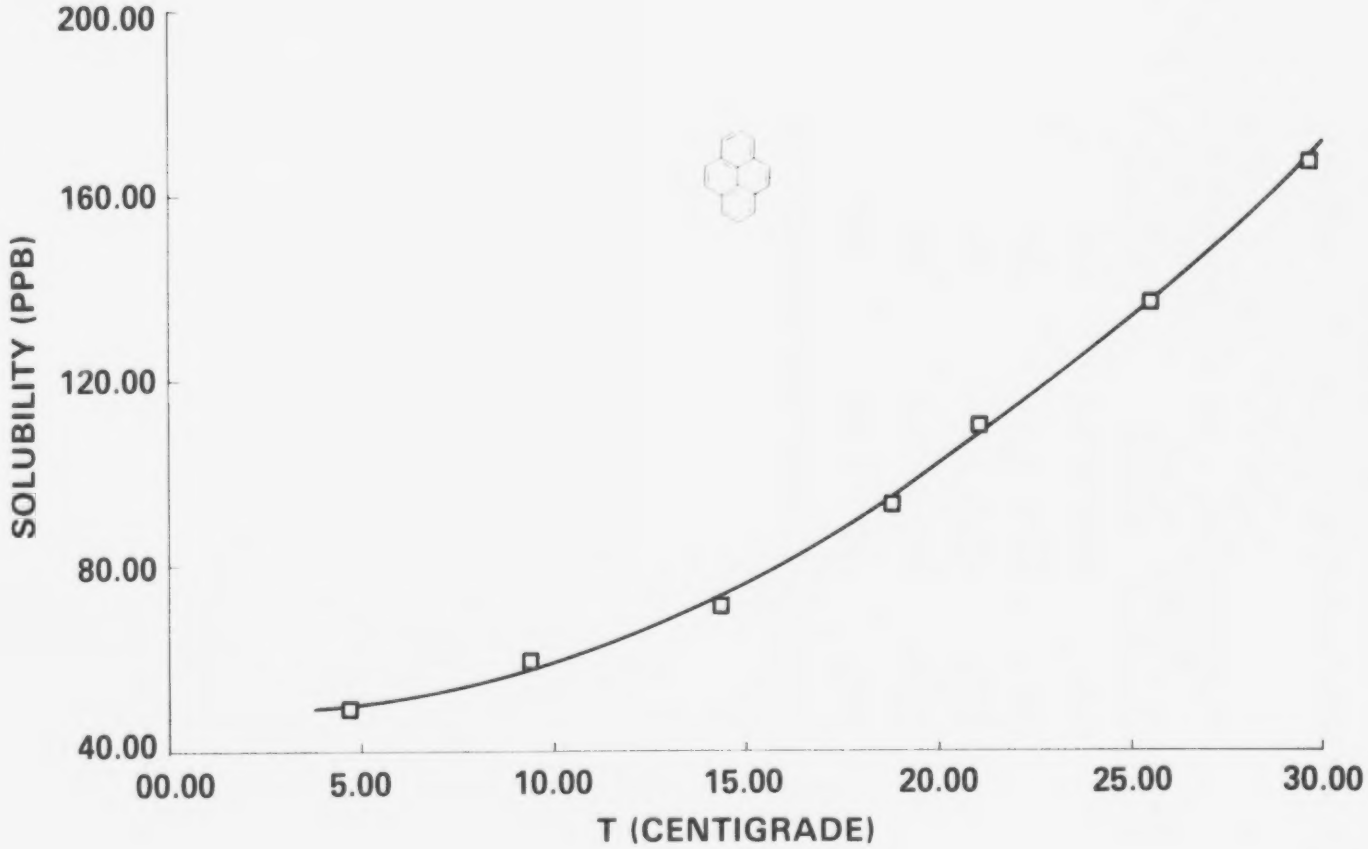


FIGURE B-9. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF PYRENE.

TABLE B-9. PYRENE

Solubility = $-0.0011t^3 + 0.2007t^2 - 1.051t + 50.2$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-7})	(µg/kg)	Concentration* Calculated (µg/kg)
29.9	8.39	170 ± 1	170
25.5	6.73	136 ± 2	136
21.2	5.37	109 ± 1	108
18.7	4.61	93.3 ± 1.0	93.7
14.3	3.56	72.0 ± 1.0	73.1
9.5	2.89	58.5 ± 0.6	57.4
4.7	2.43	49.2 ± 0.1	49.5

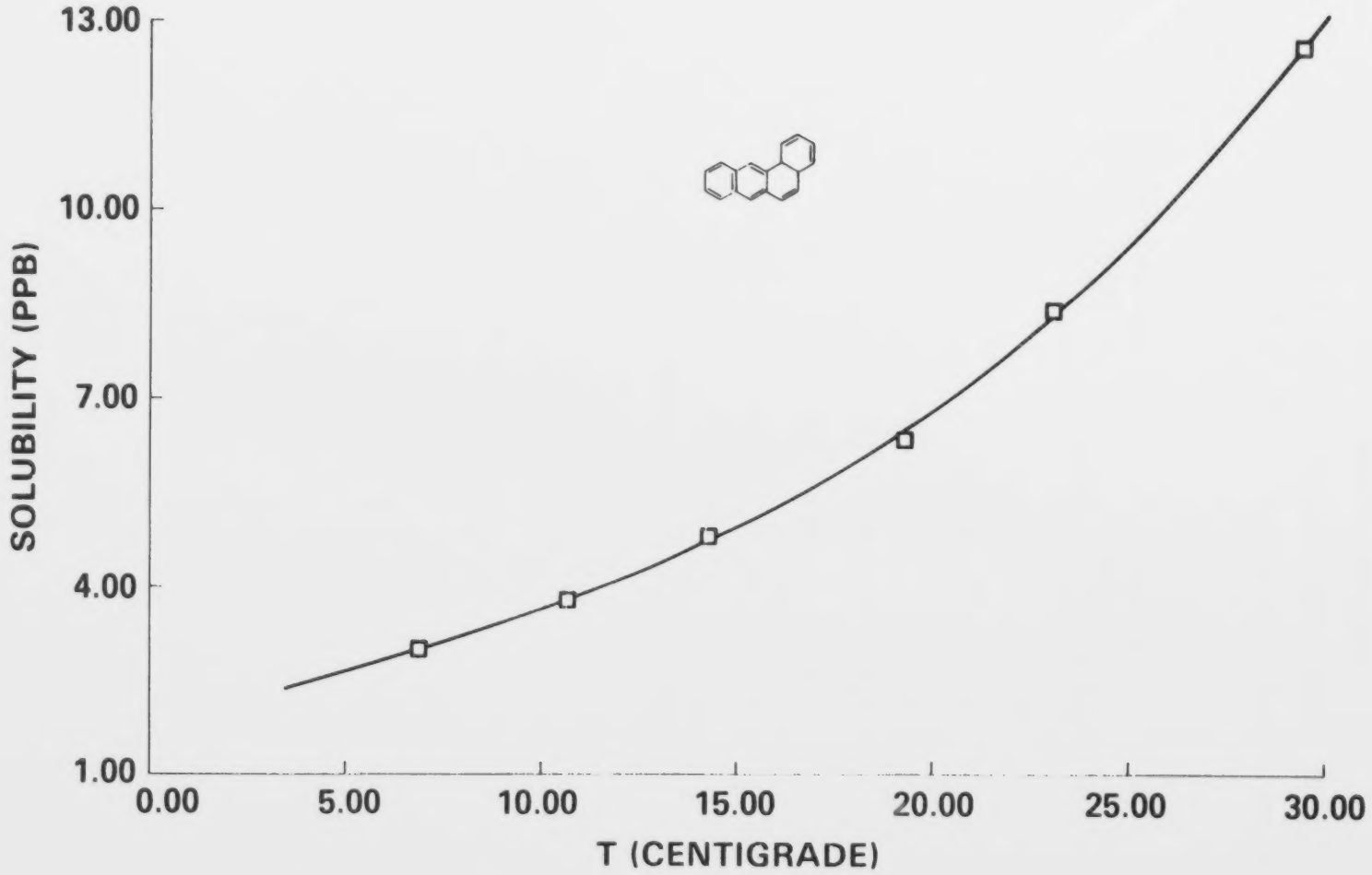


FIGURE B-10. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF 1, 2 BENZANTHRACENE.

TABLE B-10. 1,2-BENZANTHRACENE

Solubility = $0.0003t^3 - 0.0031t^2 + 0.1897t + 1.74$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-8})	(µg/kg)	Concentration* Calculation (µg/kg)
29.7	5.58	12.7 ± 0.2	12.8
23.1	3.67	8.37 ± 0.03	8.28
19.3	2.77	6.33 ± 0.02	6.47
14.3	2.10	4.79 ± 0.02	4.72
10.7	1.66	3.78 ± 0.05	3.79
6.9	1.31	2.99 ± 0.10	3.00

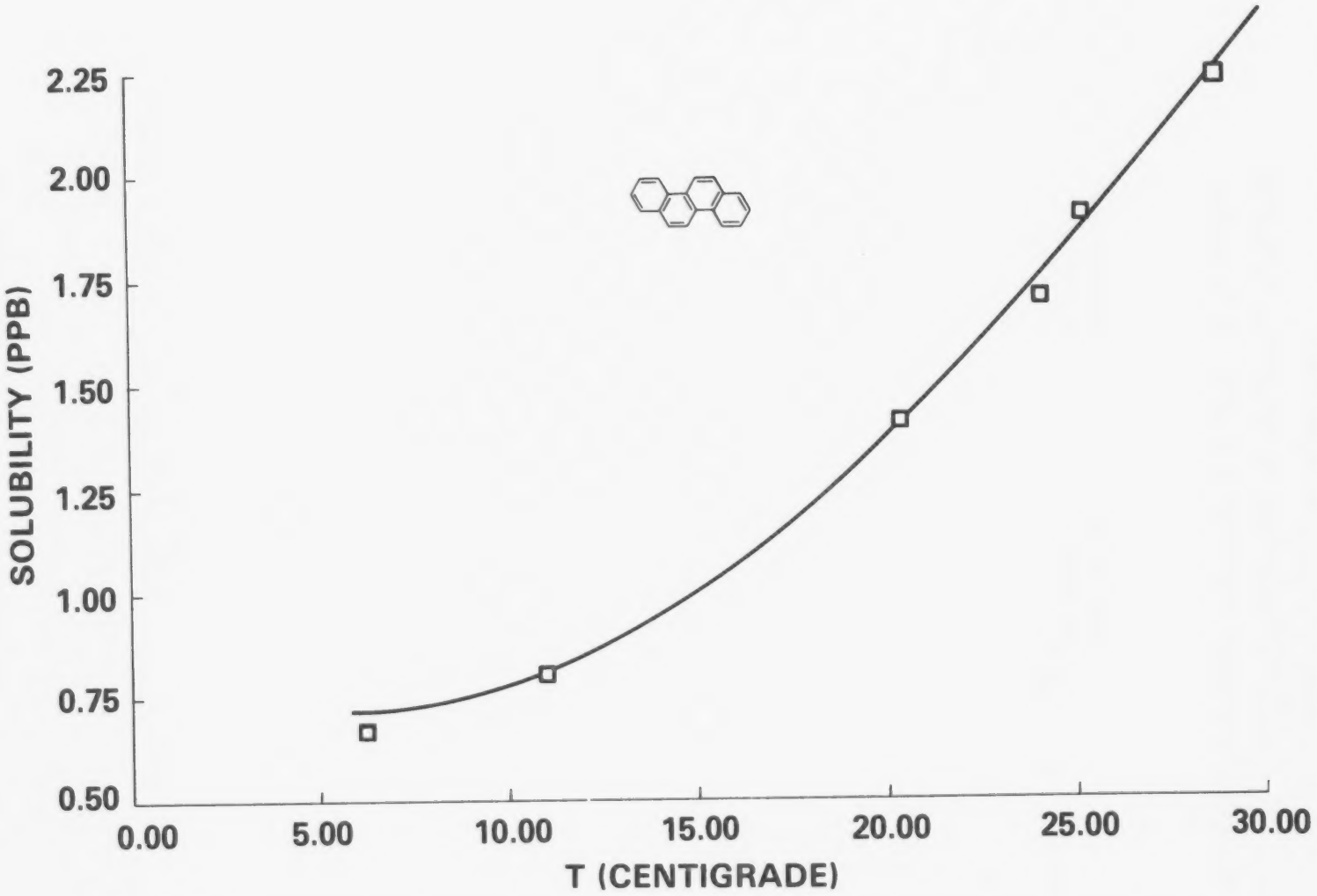


FIGURE B-11. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF CHRYSENE.

TABLE B-11. CHRYSENE

Solubility = $0.0024t^2 - 0.0144t + 0.69$ (µg/kg)*

t (°C)	Concentration Measured (mol/liter x 10^{-9})	(µg/kg)	Concentration* Calculation (µg/kg)
28.7	9.68	2.21 ± 0.02	2.23
25.3	8.28	1.89 ± 0.03	1.84
24.0	7.36	1.68 ± 0.03	1.71
20.4	6.13	1.40 ± 0.02	1.38
11.0	3.50	0.80 ± 0.02	0.82
6.5	3.10	0.71 ± 0.02	0.69

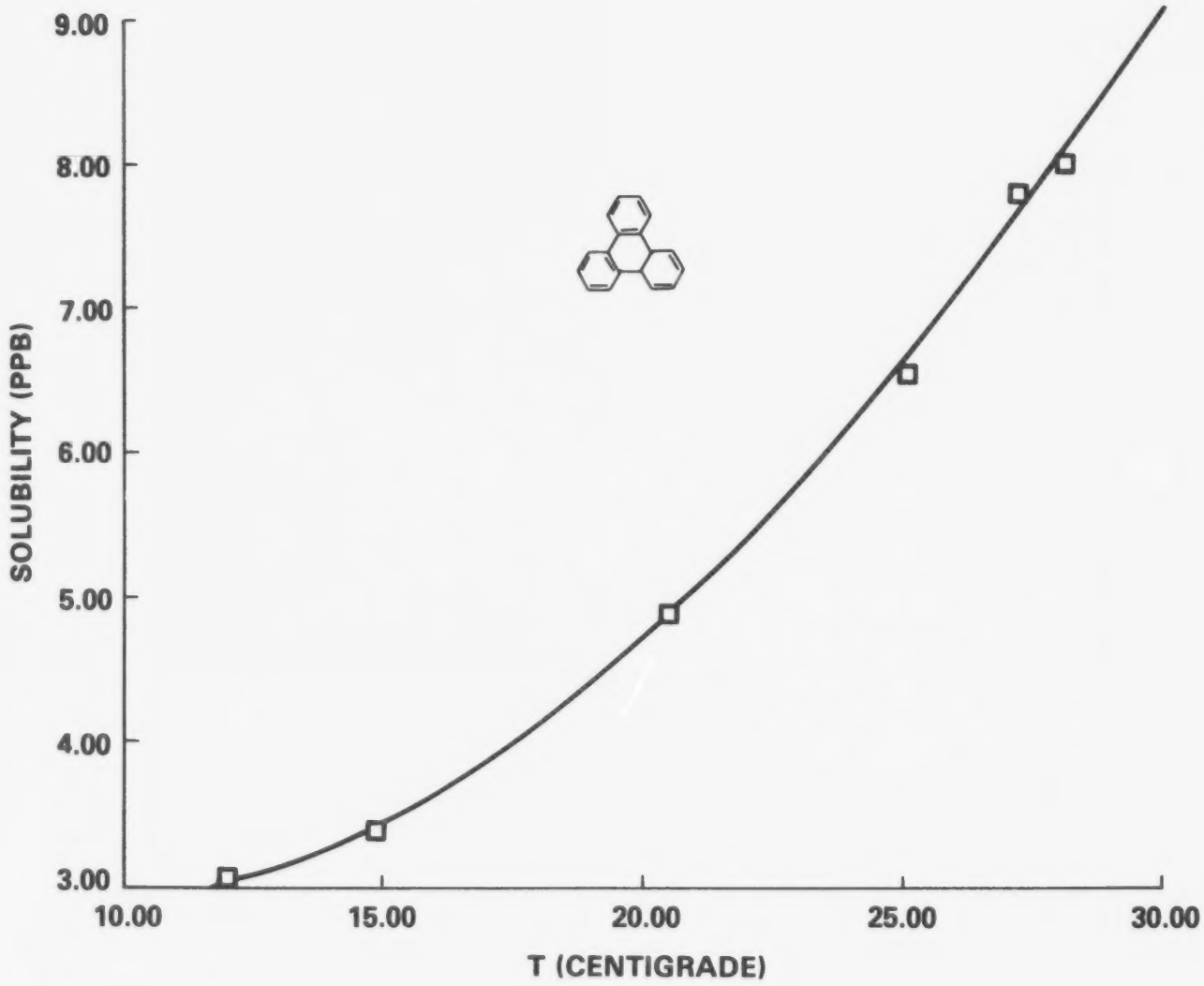


FIGURE B-12. TEMPERATURE DEPENDENCE OF THE AQUEOUS SOLUBILITY OF TRIPHENYLENE.

TABLE B-12. TRIPHENYLENE

Solubility = $-0.0002t^3t + 0.0250t^2 - 0.4250t + 4.89$

t (°C)	Concentration Measured (mol/liter x 10^{-8})	(µg/kg)	Concentration* Calculation (µg/kg)
28.2	3.55	8.11 ± 0.11	8.10
27.3	3.35	7.65 ± 0.09	7.67
20.5	2.14	4.89 ± 0.05	4.88
14.8	1.49	3.39 ± 0.06	3.40
12.0	1.33	3.03 ± 0.02	3.03
8.0	1.18	2.99 ± 0.08	2.98